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THE HYDROGENOLYSIS OF 3-HYDROXYMETHYLINDOLE AND OTHER INDOLE DERIVATIVES WITH LITHIUM ALUMINUM HYDRIDE¹

By EDWARD LEETE² AND LÉO MARION

ABSTRACT

Indole-3-aldehyde, indole-3-carboxylic acid and its ethyl ester were reduced by excess lithium aluminum hydride to skatole. The expected reduction product, 3-hydroxymethylindole, was obtained by the action of sodium hydroxide on gramine methiodide. It and its alkyl ethers were readily reduced to skatole. 3-Hydroxymethylindole underwent self-condensation to 3,3'-di-indolylmethane in neutral and alkaline media, and with acidic reagents was converted to an oxygen-free polymeric substance. The mechanism of these reactions and of the hydrogenolysis is discussed.

In the course of the investigation of various indole alkaloids anomalous products were obtained on reduction of 3-substituted indole derivatives with lithium aluminum hydride. Thus the action of this reagent on simple indole compounds was investigated with the rather surprising result that indole-3-carboxylic acid, its ethyl ester, and indole-3-aldehyde were reduced in ether solution under very mild conditions to skatole. It was also found that 3-acetylindole was reduced to 3-ethylindole.

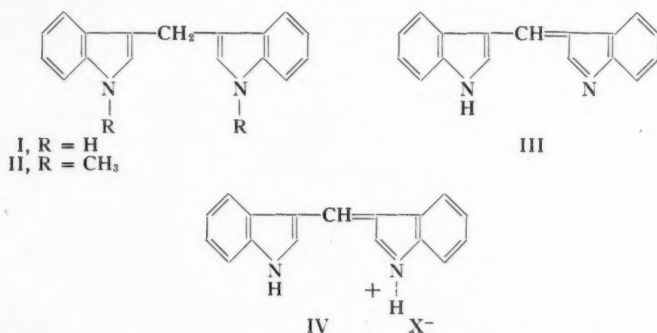
There have been a few isolated reports of the hydrogenolysis of acids and carbonyl compounds with lithium aluminum hydride to methyl or methylene groups. Witkop (40) found that an *o*-aminoketone (*spiro*cyclopentane-1,2'-pseudindoxyl) was reduced to an oxygen-free amine. Conover and Tarbell (7, 8) showed that various benzene and thiazole acids and carbonyl derivatives underwent hydrogenolysis when there was an amino group *ortho* or *para* to the group being reduced. Jones and Kornfeld (15) reported the hydrogenolysis of a carbethoxy group to a methyl in a pyridine derivative. Many of these reductions, however, were carried out for a prolonged time and at a high temperature, and it was possible to isolate the expected alcohol by employing less vigorous conditions. But with 3-carbethoxyindole, even when less than the theoretical amount of lithium aluminum hydride to cause reduction to the alcohol was employed, the only products isolated were skatole and unreduced ester. It was thus of interest to prepare by another method the 3-hydroxymethylindole which was apparently very readily reduced by lithium aluminum hydride.

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²Holder of a Postgraduate Travelling Fellowship from the Goldsmiths' Company of London, England.

This compound was first obtained by Mingoia (23) by the action of trioxymethylene on indole magnesium bromide. He described it as a stable substance melting at 158°. Repetition of this experiment yielded only high melting glassy material. Madinaveitia (21), who claimed to have obtained it by the action of methyl iodide in methanol on gramine and by the catalytic reduction of indole-3-aldehyde, described it as a substance very sensitive to acids melting at 90°. All attempts to hydrogenate indole-3-aldehyde with a variety of catalysts were unsuccessful in our hands. Derivatives of 3-hydroxymethylindole have been recorded in the literature (14, 29, 31) but they were not well characterized and their instability in air was noted. 2-Hydroxymethylindole and its derivatives have recently been prepared (12, 39) by the reduction of the corresponding carboxy compound with lithium aluminum hydride. Thus the hydroxymethyl group is apparently stable to attack by this reagent when in the 2-position of the indole nucleus. This has also proved to be the case with more complex indole derivatives (2). The ON-diacetyl derivative of 3-hydroxymethylindole has recently been prepared by the action of acetic anhydride and sodium acetate on gramine (11). Attempted hydrolysis of this ON-diacetyl derivative with boiling 10% sodium hydroxide yielded a resinous product from which we isolated an oxygen-free compound. The analytical figures suggested that this compound might be 3,3'-di-indolylmethane (I), a suggestion supported by its ultraviolet absorption spectrum which was similar to that of skatole (Fig. 1). The identity was confirmed by direct comparison with an authentic sample of 3,3'-di-indolylmethane synthesized from indole, paraformaldehyde, and zinc chloride. This compound obtained by the reduction of di-indolylmethine (III) was recorded briefly (26) without mention of any properties. It is a colorless substance very sensitive to acids



in the presence of air, rapidly becoming deep red in color presumably due to the formation of di-indolylmethine salts (urorosein) (IV)(13). Hydrolysis of ON-diacetyl-3-hydroxymethylindole with sodium hydroxide in methanol at room temperature leads to the formation of 3-methoxymethylindole and in ethanol to 3-ethoxymethylindole. Treatment with hydrochloric acid produced a dark red resinous mass. From these results it was apparent that 3-hydroxymethylindole was unstable in hot alkali and sensitive to acids.

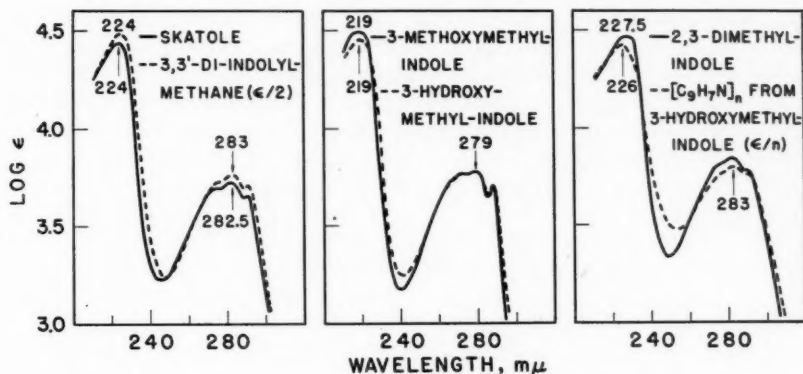


FIG. 1. Ultraviolet absorption spectra taken in 95% ethanol with a Beckman quartz spectrophotometer.

The nucleophilic attack of gramine methiodide by hydroxide ions appeared to be a possible route to 3-hydroxymethylindole, the cationoid activity of this quaternary salt being well known (11, 34, 36, 37). Accordingly an aqueous solution of authentic gramine methiodide (11) was shaken in the presence of ether with sodium hydroxide. The ether layer was found to contain 3-hydroxymethylindole. A small quantity of substance insoluble both in water and ether was also obtained in this reaction (see experimental). The 3-hydroxymethylindole, obtained in 70% yield, melted at 99–100°. The authenticity of the product was confirmed by the analytical results, molecular weight determination, and the similarity of its ultraviolet spectrum with that of 3-methoxymethylindole (Fig. 1). Its infrared absorption spectrum in nujol suspension showed an intense peak at 3360 cm^{-1} due to the NH stretching vibration, and a broad peak at 3270 cm^{-1} presumably due to a hydrogen bonded hydroxyl group. A peak similar to the former, attributable to the NH stretching vibration, was present in the infrared spectra of skatole (3395 cm^{-1}), 2,3-dimethylindole (3370 cm^{-1}), and 3,3'-di-indolylmethane (3395 cm^{-1}), whereas the latter broad absorption peak was absent in the spectra of these alkyl indoles.

3-Hydroxymethylindole was a relatively unstable substance slowly becoming brown in air. In boiling water in which it was appreciably soluble, it underwent self-condensation giving rise to the sparingly soluble 3,3'-di-indolylmethane (I) which separated out of the hot solution. This property explains the failure to obtain 3-hydroxymethylindole by the alkaline hydrolysis of its acetyl derivative and recalls the self-condensation of the 2-hydroxymethylpyrroles to give dipyrromethanes (9). The production of 1,1'-dimethyl-3,3'-di-indolylmethane (II) on boiling 1-methylgramine methiodide with sodium hydroxide (35) is presumably due to the intermediate formation of 1-methyl-3-hydroxymethylindole which then undergoes self-condensation. Attempts to acylate 3-hydroxymethylindole or to prepare its picrate were unsuccessful and resulted in considerable darkening of the reaction mixtures. 3-Hydroxymethylindole

was also found to be very sensitive to acids. Thus, addition of hydrochloric acid to its aqueous solution resulted in the separation of an amorphous white precipitate which slowly became pink in the acid medium, but was quite stable after addition of ammonia to the suspension. This precipitate could not be induced to crystallize from any solvent, and it was purified by dissolving in benzene and precipitating with petroleum ether. It contained no oxygen and the analytical results were in agreement with the empirical formula C_9H_7N . The properties of the compound, its indefinite melting point and low solubility in organic solvents, indicated a polymeric substance. A structure such as IX is suggested and it is supported by the ultraviolet spectrum of the compound which is very similar to that of 2,3-dimethylindole (Fig. 1). Further evidence for such a structure is found in the infrared absorption spectrum of the polymer particularly in the region $600\text{--}800\text{ cm}^{-1}$ (Fig. 2).

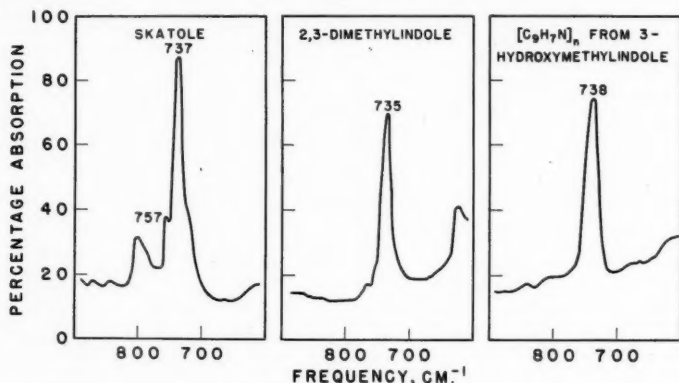
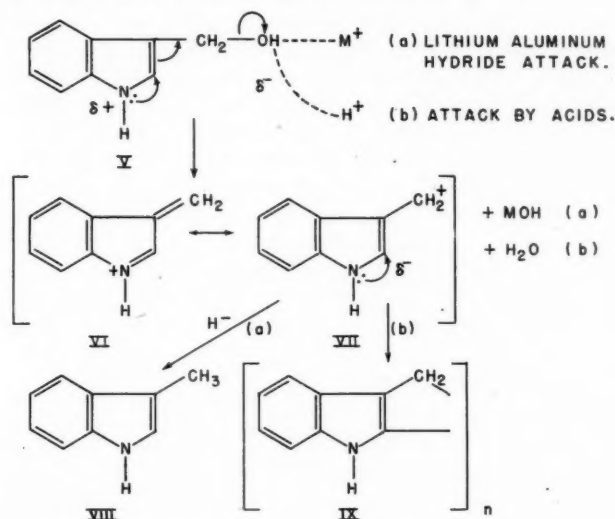


FIG. 2. Infrared absorption spectra measured as nujol mulls on a Perkin-Elmer double beam infrared spectrophotometer, Model 21 with sodium chloride prism.

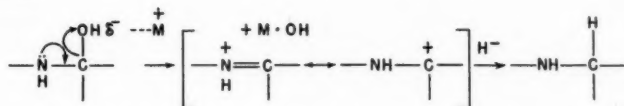
The absorption in this region has been attributed to the out-of-plane bending vibration of the CH bonds in an aromatic system (1, 6). The strong absorption at $735\text{--}738\text{ cm}^{-1}$ has been assigned to the CH vibrations in an *ortho* substituted benzene ring as in indole. It has also been found that an absorption peak at 757 cm^{-1} always occurs in alkyl indoles in which the 2-position is unsubstituted (e.g. skatole), so that this peak may be tentatively assigned to the out-of-plane bending vibration of the CH bond in the 2-position of the indole nucleus. As shown in Fig. 2 this absorption peak is absent in both the spectra of 2,3-dimethylindole and of the polymeric compound. The infrared absorption spectrum shows the expected peak at 3370 cm^{-1} due to the NH stretching vibration.

As expected, 3-hydroxymethylindole was readily reduced by lithium aluminum hydride to give skatole. It was not, however, reduced in alcohol solution by hydrogen in the presence of Adams' catalyst. Its methyl and ethyl ethers were also reduced to skatole by lithium aluminum hydride. This reagent apparently acts as a nucleophilic reagent furnishing in solution anions such

as AlH_4^- (5) or actually the hydride anion (H^-), at least in diethyl ether solution (27, 28). However, the 3-position of indole has a high electron density made evident from its chemical properties and indicated by molecular orbital calculations (20). This high electron density at the 3-position would be expected to retard attack by the hydride anion, and it is suggested that the first attack is by a positive ion (M^+) such as Li^+ or AlH_4^+ eliminating the hydroxyl group to form in the ether solution a nonionized salt $\text{M}\cdot\text{OH}$ and leaving the carbonium cation ($\text{VI} \leftrightarrow \text{VII}$) which rapidly picks up a hydride anion to give the final hydrogenolysis product (VIII). A similar mechanism has been proposed for the reduction of the *ortho* and *para* amino aromatic acids and carbonyl derivatives (7). It is considered that the attack by acids proceeds by a similar mechanism, the proton extracting the hydroxyl group and thus giving rise to the carbonium ion VII which undergoes self-condensation at the free electronegative 2-position to produce the polymer IX .



The facile reduction of amino-aldehydes with lithium aluminum hydride to give oxygen-free amines (10, 24, 25) presumably proceeds by a similar mechanism.



3-Hydroxymethylindole may be regarded as the vinylogue of an amino-aldehyde. The reduction of the tosyl derivatives of alcohols (16, 17, 18, 19, 30, 33) with lithium aluminum hydride has also been interpreted (33) as proceeding through an elimination of the tosylate group to leave a carbonium cation which then picks up a hydride anion from the solution.

EXPERIMENTAL³*O,N-Diacetyl-3-hydroxymethylindole*

This was prepared essentially by the method of Geissman and Armen (11) with, however, a marked increase in yield. Gramine (10 gm.) and dry sodium acetate (20 gm.) were refluxed in a metal bath with freshly distilled acetic anhydride (100 ml.) for four hours. The mixture was cooled and poured into a stirred mixture of ice and sodium carbonate solution. After stirring for one hour the yellow amorphous precipitate was filtered off, washed, and dried *in vacuo* (12.3 gm., 88% yield). Crystallization from ethanol (charcoal) yielded the acetyl derivative as pale yellow needles, m.p. 89–90°, (11.0 gm.).

*Attempted Hydrolysis of O,N-Diacetyl-3-hydroxymethylindole**(a) With Aqueous Sodium Hydroxide (3,3'-Di-indolylmethane I)*

The diacetyl derivative (5.0 gm.) was refluxed with 10% sodium hydroxide solution (200 ml.) on a metal bath for 18 hr. A brown tar separated on the surface of the liquid; it was removed by decantation and on cooling set to a solid (2.96 gm.). This product was dissolved in hot benzene (20 ml.) and the filtered solution on cooling deposited a brown amorphous substance (1.03 gm.), m.p. 135–160°, which was crystallized from benzene (charcoal). 3,3'-Di-indolylmethane thus obtained consisted of colorless plates melting at 164–165°, either alone or in admixture with an authentic synthetic sample. Calcd. for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37; mol. wt., 246.3. Found: C, 83.11; H, 5.67; N, 11.42%; mol. wt. (Rast) 251. In contrast to skatole it was almost odorless and sublimed unchanged *in vacuo* (150° at 10^{-4} mm.) very slowly. In air it became brown and on treatment with acids became pink and finally bright red. Attempts to prepare a picrate or an acetyl derivative were unsuccessful. In the Ehrlich test it gave a red color which became orange-red on standing.

(b) With Alcoholic Sodium Hydroxide

To a suspension of *O,N*-diacetyl-3-hydroxymethylindole (5.0 gm.) in ethanol (25 ml.), 10% sodium hydroxide (17 ml.) was added. All the diacetyl derivative dissolved and in the course of about half an hour colorless prisms had separated, the quantity of which was increased by the addition of water. The precipitated substance was filtered and dried (3.27 gm.), m.p. 60–65°, and recrystallized from petroleum ether (b.p. 50–80°) from which it separated as colorless prismatic needles, m.p. 63–64°, not depressed by admixture with 3-ethoxymethylindole (3, 11). Calcd. for $C_{11}H_{13}ON$: C, 75.40; H, 7.48. Found: C, 75.32; H, 7.69%. When the reaction was carried out in methanol the product was 3-methoxymethylindole, obtained as colorless prismatic needles from benzene – petroleum ether, m.p. 94–95°.

3,3'-Di-indolylmethane (I)

To indole (4.0 gm.) and paraformaldehyde (0.2 gm.) melted together on the steam bath, powdered zinc chloride (1.0 gm.) was added and the mixture heated on the steam bath for 15 hr. After cooling, unchanged indole was extracted with petroleum ether and the residue extracted with hot benzene. The benzene extract on cooling deposited an amorphous solid (0.34 gm.),

³All melting points are corrected.

m.p. 138–140°, which crystallized from benzene and after several recrystallizations from the same solvent consisted of colorless plates (0.12 gm.), m.p. 164–165°. The melting point of this sample of 3,3'-di-indolylmethane was not depressed by admixture with the product obtained by the hydrolysis of O,N-diacetyl-3-hydroxymethylindole. Calcd. for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 83.34; H, 5.60; N, 11.16%.

3-Hydroxymethylindole (V)

Of several modifications the following method was found to give the highest yield of 3-hydroxymethylindole. Gramine methiodide (5.0 gm.), prepared according to Geissman and Armen (11), was dissolved in cold water (200 ml.) and added slowly to a rapidly stirred mixture of 10% sodium hydroxide (200 ml.) and ether (200 ml.). A small amount of white precipitate was produced and as soon as all the gramine methiodide had been added (10 min.) this was filtered off (0.24 gm.) and the ether layer separated from the filtrate. The residual aqueous layer was extracted several times with further quantities of ether and the combined ether extract was dried over sodium sulphate and distilled at room temperature *in vacuo*. A white crystalline solid (2.18 gm.) was left which crystallized from benzene. 3-Hydroxymethylindole thus obtained (1.54 gm., 66% of theory) consisted of colorless leaflets, m.p. 99–100°. Calcd. for C_9H_9ON : C, 73.45; H, 6.16; N, 9.52; mol. wt., 147.2. Found: C, 73.49, 73.64; H, 6.09, 6.18; N, 9.47, 9.38; mol. wt. (Rast) 150. Variations in this experimental procedure such as the reverse addition of the sodium hydroxide to the gramine methiodide lead to an increase in the amount of insoluble white precipitate obtained. This product was sparingly soluble in alcohol and almost insoluble in other organic solvents. It melted indefinitely at 190–210°, contained iodine, and may have been formed by the attack of gramine methiodide by the 3-indolylmethylene carbonium ion.

3-Hydroxymethylindole was readily soluble in alcohol and ether, moderately soluble in cold water, and sparingly soluble in petroleum ether. It gave a reddish violet color in the Ehrlich test. Attempts to prepare a picrate or acyl derivatives resulted only in the formation of amorphous resinous products.

Self-condensation of 3-Hydroxymethylindole

(a) In Neutral Solution

3-Hydroxymethylindole (0.10 gm.) was refluxed in water (50 ml.) for six hours in a current of nitrogen which was ultimately bubbled through a solution of dimedone (5,5-dimethylcyclohexane-1,3-dione). On cooling, the solution deposited a pale brown microcrystalline product (0.056 gm.) which on crystallization from benzene afforded colorless plates, m.p. 162–163°, not depressed by admixture with 3,3'-di-indolylmethane. No precipitate was detected in the dimedone solution indicating that no formaldehyde was liberated. The aqueous solution obtained after removal of the di-indolylmethane when treated with mercuric chloride gave a white precipitate of mercurous chloride indicating the presence of formic acid.

(b) Effect of Heat

3-Hydroxymethylindole (0.20 gm.) was heated in a dry tube in a current

of nitrogen for three hours at 200°. The nitrogen was ultimately passed into a solution of dimedone in which a small amount of crystalline precipitate was produced (20 mgm.), m.p. 189–190°, either alone or in admixture with dimedone–formaldehyde condensate. The residue in the reaction tube was soluble in benzene but could not be induced to crystallize.

(c) *Effect of Alkali*

3-Hydroxymethylindole (1.0 gm.) was refluxed with 10% sodium hydroxide (100 ml.) for one hour. The solution was cooled, neutralized with carbon dioxide, and filtered. The filtered substance (0.52 gm.) was crystallized from benzene to yield glistening plates of 3,3'-di-indolylmethane, m.p. 163–164°.

(d) *Effect of Acid*

When 3-hydroxymethylindole (0.20 gm.) was dissolved in cold water (100 ml.) and concentrated hydrochloric acid (40%, 1 ml.) was added, an almost white precipitate immediately separated which became pink after a few minutes. The mixture was alkalized with ammonia, the precipitate filtered off and washed well with water. The product after drying *in vacuo* weighed 0.177 gm. and melted at 150–170°. It was boiled with benzene and the solution filtered to remove a small amount of insoluble material. To the filtrate petroleum ether was added, which caused the separation of a white precipitate, m.p. 160–200°, becoming red at 140°. Calcd. for C_9H_7N : C, 83.69; H, 5.46; N, 10.85. Found: C, 83.33, 83.47; H, 5.57, 5.52; N, 10.62, 10.49%. It was insoluble in most of the common organic solvents, sparingly soluble in ethanol, and moderately soluble in benzene.

General Method of Reduction of the Indole Derivatives with Lithium Aluminum Hydride

The indole derivative (0.5–2.0 gm.) was dissolved or suspended in sodium-dried ether (50–200 ml.) and a definite amount of lithium aluminum hydride in ether solution was added to the stirred suspension or solution. The mixture was then refluxed in a nitrogen atmosphere for one-half to three hours. After cooling, the excess lithium aluminum hydride was decomposed by the addition of wet ether, the mixture filtered, and the filtrate evaporated to dryness *in vacuo*. The residue was heated to 80° at 0.2 mm. when the alkyl indoles readily sublimed. The usual product of reduction was skatole which was characterized by its melting point (94–95°) and by the formation of its picrate, m.p. 177–178° (red fibrous needles), not depressed by admixture with authentic skatole picrate. Reduction of 3-acetylindole (32) yielded 3-ethylindole, leaflets from petroleum ether, m.p. 42°. Calcd. for $C_{10}H_{11}N$: C, 82.72; H, 7.64. Found: C, 82.41; H, 7.52%. The picrate was obtained as red needles from benzene, m.p. 120° in agreement with that recorded in the literature (4). Details of the reduction of the indole derivatives are summarized in Table I.

Attempted Catalytic Reduction of 3-Hydroxymethylindole

3-Hydroxymethylindole (0.100 gm.) was shaken in ethanol (20 ml.) with freshly reduced Adams' catalyst (0.100 gm.) for six hours in the presence of

TABLE I
REDUCTION EXPERIMENTS

Compound*	Time of reflux in hours	Molecular equivalents of LiAlH ₄ used**	Reduction product (yield)
Indole-3-aldehyde (38)	3	2	Skatole, 84%
Indole-3-carboxylic acid (22)	3	3	Skatole, 67%
3-Carbethoxyindole (22)	0.5	2	Skatole, 92%
3-Carbethoxyindole (22)	0.5	0.5	3-Carbethoxyindole, 90%
			Skatole, 5%
3-Acetylindole (32)	3	2	3-Ethylindole, 72%
3-Hydroxymethylindole	0.5	2	Skatole, 87%
3-Methoxymethylindole	3	2	Skatole, 71%
3-Ethoxymethylindole	0.5	1	Skatole, 80%

* Numbers after the compounds are references to methods of preparation of those indole derivatives which are not described in the experimental.

** The strength of the lithium aluminum hydride solution was determined by measuring the volume of hydrogen evolved when a known volume of the solution was treated with cold water.

hydrogen. No hydrogen, however, was absorbed and 3-hydroxymethylindole was isolated unchanged from the reaction mixture.

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SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS

VII. DEUTERATED 3-PENTANONES¹

BY L. C. LEITCH² AND A. T. MORSE²

ABSTRACT

The following deuterated 3-pentanones were synthesized, in some cases by modifications of the methods reported in the literature, and in others by deuterium exchange:

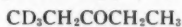
3-pentanone-*d*₁₀, 3-pentanone-1,5-*d*₆,
3-pentanone-2,4-*d*₄, 3-pentanone-1-*d*₃,
3-pentanone-1,2,4-*d*₇, and 3-pentanone-1,2-*d*₅.

INTRODUCTION

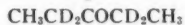
The deuterated pentanones I to VI were recently synthesized for investigations in chemical kinetics (12) and infrared spectroscopy (11).



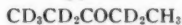
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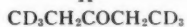
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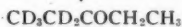
II



V



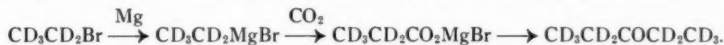
III



VI

These compounds, as well as the starting materials and intermediates from which they were obtained, are all believed to be new. They were prepared by well-known reactions modified on account of the peculiar difficulties associated with the synthesis of organic deuterium compounds.

Ivanoff (5) has reported the synthesis of several aliphatic ketones from alkyl halides without isolating the intermediate acids. In the present work 3-pentanone-*d*₁₀ (I) was prepared from ethyl-*d*₅ bromide by the same reactions:



The important feature of this synthesis is that the isolation of deuterated propionic acid is avoided, rendering unnecessary either the subsequent preparation of the barium salt or the replacement of hydrogen by deuterium in the carboxyl group before pyrolysis.

Preliminary experiments with ordinary ethyl bromide indicated that the yield of 3-pentanone-*d*₁₀ depended largely upon the design of the reactor in which the pyrolysis of propionoxymagnesium bromide was carried out. In a reactor of the dimensions specified by Ivanoff, the yields of 3-pentanone-*d*₁₀ were consistently 70% or more based on the ethyl bromide, as he had claimed.

Ethyl-*d*₅ bromide was prepared by photochemical addition of deuterium bromide to ethylene-*d*₄ which was obtained as described in an earlier paper of this series (7). The halide contained 96.8 mole % C₂D₅Br. The vapor pressure

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of ethyl- d_5 bromide was measured at several temperatures as shown in Table I. These data were used to plot the vapor pressure of ethyl- d_5 bromide shown in Fig. 1. The line representing the vapor pressure of normal ethyl bromide was plotted from values reported in International Critical Tables. The Grignard reagent was prepared from the halide and carbonated in the

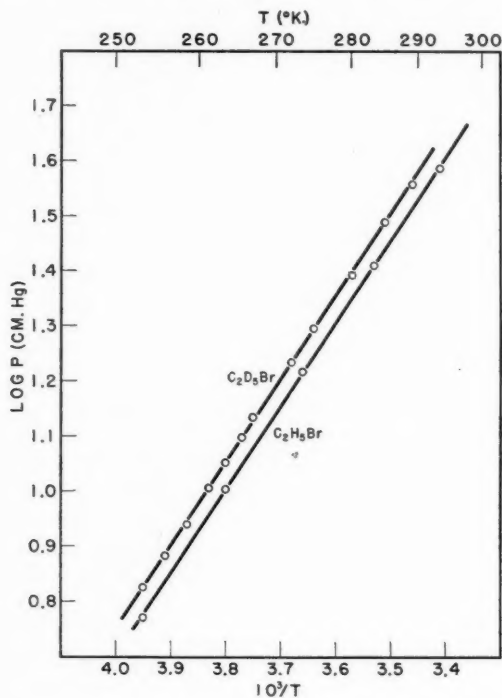


FIG. 1.

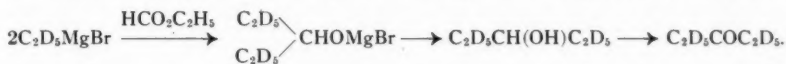
TABLE I
VAPOR PRESSURES (P) OF ETHYL BROMIDE AND ETHYL- d_5 BROMIDE

C_2H_5Br		C_2D_5Br		C_2D_3Br	
Temp., °C.	P , cm.	Temp., °C.	P , cm.	Temp., °C.	P , cm.
-20.0	5.90	-20.0	6.70	-6.0	13.65
-10.0	10.10	-17.0	7.63	-1.0	17.14
0.0	16.50	-14.5	8.69	+1.5	19.72
+10.0	25.69	-12.0	10.14	+7.0	24.66
+20.0	38.59	-10.0	11.27	+12.0	30.83
		-7.5	12.53	+16.0	36.14

usual way. On pyrolysis, 3-pentanone- d_{10} (I) was obtained which analyzed 70.4 mole % $C_5D_{10}O$ by mass spectrometry.

The 3-pentanone- d_{10} obtained by direct synthesis was further enriched in deuterium by repeated exchange with deuterium oxide containing a trace of anhydrous sodium carbonate. The final product analyzed 85.8 mole % $C_5D_{10}O$. Since only the exchange of hydrogen atoms adjacent to a carbonyl group in ketones is base-catalyzed, it would seem that most of the residual hydrogen is now in the methyl groups. The appearance of hydrogen in these positions indicates exchange took place during pyrolysis—a circumstance considered irremediable.

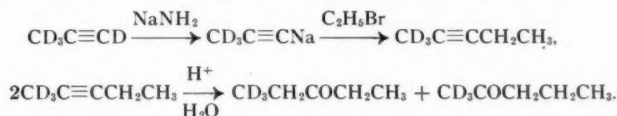
An alternative synthesis of 3-pentanone- d_{10} is the sequence of reactions:



The deuterated pentanol was obtained in 80% yield as described by Lewis (9). In order to prevent the loss of deuterium in the methylene groups by exchange, the oxidation of the pentanol must be carried out in a neutral anhydrous medium. These conditions were met by employing a modified Oppenauer oxidation (6). When the alkoxide of the deuterated pentanol was treated with benzophenone, 3-pentanone- d_{10} , which analyzed 59.1 mole % $C_5D_{10}O$, was formed. The deuterium content was raised to 98.92 atom % or 90.5 mole % 3-pentanone- d_{10} by three exchanges with deuterium oxide in the presence of sodium carbonate.

3-Pentanone-2,4- d_4 (II) was prepared by exchanging ordinary 3-pentanone with deuterium oxide in the same manner. After 10 exchanges, the deuterium content remained practically constant at 92.5 mole % $CH_3CD_2COCDC_2H_3$. Conversely, 3-pentanone- d_{10} was exchanged with ordinary water containing a trace of carbonate to give 3-pentanone-1,5- d_6 (III). The final product analyzed 88.7 mole % $CD_3CH_2COCH_2CD_3$.

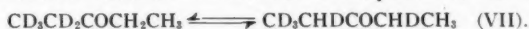
3-Pentanone-1- d_3 (IV) was prepared by the following reactions:



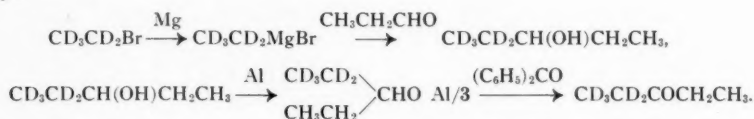
The starting material, propyne- d_4 , was prepared by the method of Leitch and Renaud (8) and converted into 2-pentyne-1- d_3 by alkylation of the sodium derivative as described by Greenlee (3). Hydration of the alkyne gave a mixture of isomeric pentanones (10) which were separated by means of saturated aqueous sodium bisulphite (4). The methyl ketone forms an addition compound about twenty times faster than the 3-pentanone.

The pentanone (V) was obtained by exchanging (IV) with alkaline deuterium oxide. It analyzed 85.4 mole % $CD_3CD_2COCDC_2H_3$.

The synthesis of (VI) was attempted, partly to complete the series and partly to find out whether or not such a compound would equilibrate thus:



The desired compound was obtained almost isotopically pure in the following way:



Deuterated 3-pentanol-1,2- d_5 was made in the usual manner from ethyl- d_5 magnesium bromide and propionaldehyde. In order to avoid the acid- or base-catalyzed rearrangement of the ketone shown in (VII), the pentanol had to be oxidized in an anhydrous neutral medium. This objective was realized by again employing a modified Oppenauer oxidation (6). When the alkoxide of 3-pentanol-1,2- d_5 was treated with benzophenone, 3-pentanone-1,2- d_5 was formed. The mass spectrum of the ketone showed 86.5 mole % $\text{C}_5\text{H}_5\text{D}_5\text{O}$; from an examination of the fragments, however, it appeared that the product contained a small amount of rearranged ketone.

Exchange with deuterium oxide gave the ketone (V) while exchange with ordinary water gave ketone (IV). Mass spectra indicated that the isotopic purity of these compounds exceeded that of the products obtained from propyne- d_4 .

EXPERIMENTAL

Ethyl- d_5 Bromide

Ethylene- d_4 was prepared as described in an earlier paper (7). The reactor there described was fitted with a quartz window and, after evacuation, deuterium bromide and ethylene- d_4 were introduced in a ratio of 1:1. The mixture was irradiated with ultraviolet light from a Hanovia lamp. A trap kept at -40°C . was placed under the receiver at the bottom of the reactor to condense the ethyl- d_5 bromide as it was formed. The ethyl- d_5 bromide was washed with ice-cold water and distilled on a vacuum line, first through soda-lime and then through phosphorus pentoxide. The yield of product analyzing 96.8 mole % (99.3 atom % D; n_D^{20} 1.4211) was nearly quantitative. Its vapor pressure was measured between -20°C . and $+20^\circ\text{C}$. in an apparatus similar to that used by Booth and Swinehart (1).

3-Pentanone- d_{10} (I) (via Pyrolysis)

Ethyl- d_5 magnesium bromide was prepared by adding slowly, with stirring, a solution of 15 ml. of ethyl- d_5 bromide in 25 ml. of absolute ether to 5.0 gm. of magnesium turnings suspended in 50 ml. of absolute ether. After the reaction mixture had been refluxed for 45 min., it was cooled to -20°C . while dry argon was passed through the apparatus; dry carbon dioxide was then introduced during one hour. Finally, the reaction mixture was brought to room temperature under an atmosphere of argon. After the ether was distilled off, the residue was gradually heated to 200°C . and kept at that temperature for one hour while argon was passed through the apparatus. When the residue had cooled to room temperature, it was rapidly transferred, preferably in a dry box, to a reactor of the dimensions specified by Ivanoff

(5). It was slowly heated to 250°C. under reduced pressure to remove traces of ether and, after a Dewar flask of dry ice and acetone at -78°C. had been placed under the receiver, the temperature of the reactor was slowly raised to 380°C. and kept there for one hour. The apparatus was then filled with argon and allowed to cool.

The crude deuterated pentanone in the trap was shaken with 10 ml. of deuterium oxide and distilled off on the vacuum line through Drierite into a receiver cooled in dry ice and acetone. Yield: 6.9 gm. (74%), n_D^{20} 1.3890. It analyzed 70.4 mole % $C_5D_{10}O$ (94.9 atom % D).

It was further enriched in deuterium by exchange at 80°C. with an equal volume of deuterium oxide containing 10 mgm. of anhydrous sodium carbonate in a tube with a break-off seal. The transfer of deuterium oxide and 3-pentanone- d_{10} before and after each exchange was made on a vacuum manifold so that at no time were the reactants exposed to atmospheric moisture. After four exchanges, the 3-pentanone- d_{10} analyzed as follows:

$C_5D_{10}O$	85.8 mole %
C_5D_9HO	8.80 mole %
$C_5D_8H_2O$	3.64 mole %
$C_5D_7H_3O$	0.8 mole %
n_D^{20} 1.3889.	

This corresponds to a deuterium content of 97.2 atom %. The residual hydrogen in the methyl groups would not be exchangeable for deuterium under the conditions employed.

3-Pentanol-1,2,4,5- d_{10}

A stirred solution of ethyl- d_5 magnesium bromide in ether (prepared from 7.0 gm. (0.287 mole) of magnesium turnings, 31.0 gm. (0.272 mole) of ethyl- d_5 bromide, and 100 ml. of absolute ether) was cooled to -15°C. and treated with 10.5 gm. (0.142 mole) of ethyl formate over a period of 10 min. After stirring for a further period of 15 min., 30 ml. of water were slowly added, followed by a cold solution of 12 ml. of concentrated sulphuric acid in 60 ml. of water. The lower aqueous layer was drawn off, extracted with a little ether, and the ether extract added to the main portion. The residue from the ether, on fractionation, gave 10.6 gm. (0.108 mole) of deuterated 3-pentanol, b.p. 113-4.5°C., n_D^{20} 1.4050. Yield: 79.5%.

3-Pentanone- d_{10} (via Grignard Synthesis)

A mixture of the deuterated 3-pentanol (5.0 ml.), aluminum shot (0.550 gm.), and a trace of mercuric chloride was heated with a low flame under reflux on an open vacuum manifold until hydrogen ceased to be evolved. Unreacted pentanol was then recovered by distillation under reduced pressure and reused in another run. Molten benzophenone (18 gm.) was added to the alkoxide while stirring with a magnetized bar. The 3-pentanone- d_{10} was condensed in a trap elsewhere on the line, cooled to -78°C. Yield: 3.0 ml., n_D^{20} 1.3892, 94.3 atom % D. The unreacted pentanol (2.0 ml.), oxidized in the same manner, gave 0.5 ml. more of the ketone, n_D^{20} 1.3897, 93.4 atom % D. The total yield was therefore 3.5 ml. of ketone from 5.0 ml. of 3-pentanol.

This product was further enriched in deuterium by three exchanges with deuterium oxide in the presence of traces of sodium carbonate. It now analyzed:

$C_5D_{10}O$	90.5 mole %
C_5D_9HO	7.58 mole %
$C_5D_8H_2O$	1.70 mole %
$C_5D_7H_3O$	0.36 mole %
Atom % D, 98.9; n_D^{20} 1.3888	

3-Pentanone-2,4- d_4 (II)

Redistilled 3-pentanone (10 ml.) was exchanged with alkalized deuterium oxide (10 ml.) as already described until its deuterium content reached an optimum. After 10 exchanges the compound analyzed as follows:

$C_5H_5D_5O$	2.78 mole %
$C_5H_6D_4O$	92.5 mole %
$C_5H_7D_3O$	3.7 mole %
$C_5H_8D_2O$	0.78 mole %
Atom % D, 40.0; n_D^{20} 1.3918.	

3-Pentanone-1,5- d_6 (III)

3-Pentanone- d_{10} was exchanged three times with water containing a trace of sodium carbonate. The product then analyzed as follows:

$C_5D_7H_3O$	0.73 mole %
$C_5D_6H_4O$	88.7 mole %
$C_5D_5H_5O$	8.25 mole %
$C_5D_4H_6O$	2.61 mole %
Atom % D, 58.9; n_D^{20} 1.3904.	

2-Pentyne-1- d_3

Sodium amide was prepared by adding sodium (5.7 gm.) to 100 ml. of liquid ammonia in a 300 ml. round-bottomed flask with a stirrer, addition tube, and a tin spiral condenser cooled with dry ice and acetone (3). Propyne- d_4 (5.0 l.) prepared as in Reference 8 was distilled into the stirred suspension of sodium amide. Ethyl bromide (30 gm.) was added as rapidly as possible to the sodium methyl- d_3 acetylide and the reaction mixture was stirred for six hours. Water (200 ml.) and toluene (20 ml.) were added dropwise. The toluene layer was separated, treated as described by Greenlee (3), and fractionated in a short Stedman column ($\frac{3}{8}$ in. \times 18 in.). The pentyne was collected between 54 and 56°C. Yield: 91%.

3-Pentanone-1- d_3 (IV)

The pentyne (13.0 gm.) from the previous experiment was stirred at 0°C. with 69 ml. of 80% sulphuric acid for two hours and the reaction mixture was poured into ice water. The yield of mixed ketones, analyzing 37.4% 2-pentanone and 62.6% 3-pentanone, as determined by mass spectrometry, was 18.5 ml. (82% yield).

The mixed ketones were distilled on a vacuum line into a suspension of 16 gm. of sodium bisulphite in 24 ml. of water and the mixture was shaken several minutes by hand. The unreacted ketone was distilled off and collected in a trap cooled with dry ice and acetone. After repeating the treatment with water and sodium bisulphite five more times, the volume of ketone had shrunk

to 8 ml. It was then distilled through a tube containing pellets of sodium hydroxide to remove sulphur dioxide. This product gave only a trace of iodoform on standing in sodium hypoiodite solution and analyzed as follows:

$C_5H_{10}O$	3.17 mole %
C_5H_8DO	7.67 mole %
$C_5H_6D_2O$	4.92 mole %
$C_5H_7D_3O$	82.2 mole %
$C_5H_6D_4O$	0.21 mole %
Atom % D, 26.5; n_D^{20} 1.3914.	

3-Pentanone-1,2,4-d₇ (V)

3-Pentanone-1-*d*₃ (2.0 ml.) was exchanged three times with deuterium oxide (10.0 ml.) as already described. The final product analyzed as follows:

$C_5D_3H_2O$	0.045 mole %
$C_5D_7H_3O$	85.4 mole %
$C_5D_9H_4O$	7.07 mole %
$C_5D_5H_5O$	2.60 mole %
$C_5D_3H_6O$	3.1 mole %
$C_5D_3H_7O$	0.74 mole %
Atom % D, 67.3; n_D^{20} 1.3901.	

3-Pentanol-1,2-d₅

Freshly distilled propionaldehyde (10.0 ml.) was added to a solution of ethyl-*d*₅ magnesium bromide prepared as described above from 10.0 ml. ethyl-*d*₅ bromide and 3.0 gm. of magnesium, and the reaction mixture was worked up in the usual manner (2). The yield of deuterated pentanol, b.p. 111–113°C., was 10.2 ml. (71%).

3-Pentanone-1,2-d₅ (VI)

A mixture of 3-pentanol-1,2-*d*₅, aluminum shot (0.81 gm.), and a trace of mercuric chloride was heated with a low flame under reflux on an open vacuum line until hydrogen ceased to be evolved. Unreacted pentanol was then removed by distillation under reduced pressure. Molten benzophenone (25 gm.) was added to the residue of aluminum alkoxide while stirring. The 3-pentanone evolved was condensed in a trap elsewhere on the vacuum line, cooled to –78°C. The yield of product was 6.7 ml. (75%). It analyzed:

$C_5H_4D_6O$	3.72 mole %
$C_5H_3D_7O$	86.5 mole %
$C_5H_6D_4O$	6.45 mole %
$C_5H_7D_3O$	3.49 mole %
Atom % D, 49.0; n_D^{20} 1.3903.	

When this product was exchanged with alkalized deuterium oxide, it gave 3-pentanone-1,2,4-*d*₇ (V) which had been obtained as described above by an alternative method. The product now described analyzed as follows:

$C_5D_5H_2O$	0.67 mole %
$C_5D_7H_3O$	87.5 mole %
$C_5D_9H_4O$	8.55 mole %
$C_5D_5H_5O$	3.29 mole %
$C_5D_3H_6O$	1.30 mole %
Atom % D, 69.3; n_D^{20} 1.3892.	

Its deuterium content was slightly higher than that of the product obtained

from propyne- d_4 . This result is not unexpected since the ethyl- d_5 bromide was of higher isotopic purity than the propyne- d_4 .

Similarly, 3-pentanone-1,2- d_5 was exchanged with ordinary water to give 3-pentanone-1- d_3 (IV) which had also been obtained by an alternative method (p. 790). The present product analyzed:

$C_5D_4H_6O$	0.63 mole %
$C_5D_3H_7O$	96.0 mole %
$C_5D_2H_8O$	2.97 mole %
C_5DH_9O	0.57 mole %
Atom % D, 29.7; n_D^{20} 1.3912.	

The isotopic purity of this material is also superior to that of the compound described earlier for the reason mentioned above.

ACKNOWLEDGMENTS

The authors are indebted to Dr. F. P. Lossing and the Misses F. Gauthier and J. Fuller of the Mass Spectrometry Division of these laboratories, who measured the mass spectra of all the compounds.

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CRYSTALLINE XYLANS FROM STRAWS¹

By C. T. BISHOP

ABSTRACT

Hemicelluloses, extracted from barley, flax, oat, rye, and wheat straw hemicelluloses, were composed predominantly of anhydro-D-xylose units, with small amounts of L-arabinose and D-glucuronic acid. The hemicelluloses had degrees of polymerization ranging from 55 for oat to 185 for rye and were shown to be linear polysaccharides. Autoclaving in distilled water at 120°C. yielded crystalline xylans from barley, rye, and wheat straw hemicelluloses. The basic structure of the hemicellulose was maintained in the crystalline xylans, which gave identical X-ray diffraction patterns and had similar, linear structures. The crystallization procedure was found to degrade the hemicellulose, removing D-xylose, L-arabinose, and D-glucuronic acid as components of hydrolytic fragments and leaving a pure xylan one sixth to one third the length of its parent hemicellulose. Depending on uronic acid content, the five hemicelluloses in water gave pH values ranging from 2-5 with consequent variations in resistance to hydrolysis during autoclaving.

INTRODUCTION

Polysaccharides composed predominantly of anhydro-D-xylose units (xylans) are found in many natural products and have been the subjects of a number of structural investigations. The uncertainties and complexities arising from these investigations were discussed in a recent publication by Adams (1). In 1949 Yundt (17) crystallized a xylan by autoclaving a hemicellulose fraction of barley straw. The crystalline xylan was composed entirely of anhydro-D-xylose units and, based on a comparison of specific rotations, was very similar to Haworth's esparto xylan (18). However, no structural study of the crystalline xylan was made nor was the possible degradative effect of autoclaving on the hemicellulose investigated.

The purpose of the present investigation was to determine the effect of autoclaving on hemicelluloses of five cereal straws and to examine the constitutions of the xylans produced, if any.

RESULTS AND DISCUSSION

Hemicelluloses were prepared from barley, flax, oat, rye, and wheat hemicelluloses (2) as described in the experimental section. Molar compositions of the hemicelluloses are shown in Table I.

TABLE I
MOLAR COMPOSITIONS OF HEMICELLULOSES¹

Hemicellulose	D-Xylose	L-Arabinose	Uronic acid
Barley	50	6	1
Rye	16	3	1
Wheat	21	3	1
Flax	7	—	1
Oats	10	3	1

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Successive autoclavings in distilled water and separation of the products yielded crystalline xylans from barley, rye, and wheat hemicelluloses. The hemicelluloses of flax and oats were completely degraded to products soluble in 75% ethanol. Table II shows the pH values of the hemicelluloses in water and the yields of crystalline xylans obtained from each. The acid properties exhibited were inherent in the molecules because all hemicelluloses were

TABLE II
pH OF HEMICELLULOSES AND YIELDS OF CRYSTALLINE XYLAN

Hemicellulose	pH in water	Yield of crystalline xylan (% of hemicellulose)
Barley	5.0	29.4
Wheat	5.0	23.7
Rye	3.5	8.5
Oat	2.0	Nil
Flax	2.0	Nil

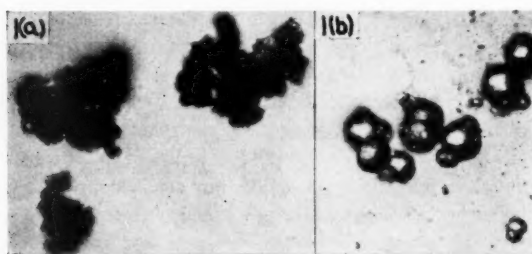


FIG. 1. (a) Wheat straw hemicellulose, (b) crystalline wheat xylan, magnification 604X.
FIG. 2. Chromatogram of ethanol solubles from autoclavings of straw hemicellulose.

prepared at the same time and by exactly the same procedures. It is also apparent that the decrease in pH of the hemicelluloses bears a direct relationship to the increase in uronic acid contents. Hydrolysis of the crystalline xylans, followed by chromatographic examination of the hydrolyzate showed that D-xylose was the only constituent sugar. No traces of L-arabinose or D-glucuronic acid originally present in the hemicellulose as single unit side chains (1) could be found, even when the papers were heavily spotted. This confirmed, by a more sensitive method, Yundt's (18) observation that crystalline barley xylan was composed entirely of anhydro-D-xylose units.

The crystallinity of the xylans was confirmed by microscopic examination and by X-ray diffraction. Photomicrographs of amorphous wheat straw hemicellulose and the crystalline xylan obtained from it are shown in Fig. 1. The X-ray powder diagrams of the three crystalline xylans were identical; the hemicelluloses gave no diffraction patterns. Crystallizations were carried out in 0.2% aqueous solutions, hence it is unlikely that the crystals were oligosaccharides because they would be soluble at that concentration. A precedent for the crystallization of a polysaccharide is found in the work of Schoch (13) who crystallized an amylose fraction from starch.

Table III shows the relative degrees of polymerization (D.P.) of the

TABLE III
D.P.'S OF HEMICELLULOSES AND CRYSTALLINE XYLANS
(Calculated from viscosity measurements $K_m = 5 \times 10^{-4}$)

	Hemicelluloses	Crystalline xylans
Barley	179	60 (1/3)
Wheat	150	33 (1/5)
Rye	185	30 (1/6)

hemicelluloses and corresponding crystalline xylans as determined by viscosity measurements on their solutions in cupriethylenediamine. Whether the values are absolute or not depends on the validity of the constant $K_m = 5 \times 10^{-4}$ (9). The results show that autoclaving degraded the hemicelluloses, shortening the chains one third to one sixth their original length. Adams and Castagne (3) have shown that approximately 50% of wheat straw hemicellulose can be obtained homogeneous in chemical constitution and molecular size. Therefore, the low yields of crystalline xylans, the complete removal of L-arabinose and D-glucuronic acid branch units, and the large (78%) decrease in D.P. make it highly probable that a degradation rather than a fractionation occurred during autoclaving.

Periodate oxidation can often be used to determine whether the structure of a polysaccharide is linear or branched (5). Table IV shows the periodate consumptions of the hemicelluloses and crystalline xylans. These results indicated the presence of linear structures because a straight chain xylan, linked 1-4 (1), would consume one mole of periodate for each anhydro-D-

TABLE IV
PERIODATE CONSUMED BY HEMICELLULOSES AND CRYSTALLINE XYLANS
(Moles periodate/mole polysaccharide)

	Hemicelluloses	Crystalline xylangs
Barley	0.92	0.94
Wheat	0.90	0.92
Rye	1.08	0.93

xylose unit, plus an extra mole at each end of the chain. In a long, straight chain the effect of end groups is diminished and periodate consumption approaches one mole per mole of polysaccharide. The similarities in periodate consumptions showed that the basic structure of the hemicellulose was maintained in the crystalline xylan. The uniformity of the specific rotations (Table V) was further confirmation of this fact and the high negative values indicated a predominance of β -glycosidic bonds.

TABLE V
SPECIFIC ROTATIONS OF HEMICELLULOSES AND CRYSTALLINE XYLANS

	$[\alpha]_D^{26}$ ($c = 1.0$ in 2% aqueous potassium hydroxide)	
	Hemicellulose	Crystalline xylangs
Barley	- 95.6°	- 85.2°
Wheat	- 81.6°	- 79.3°
Rye	- 87.1°	- 83.4°

Some features of the structures of the crystalline xylans were now evident. Based on periodate consumptions and specific rotations the crystalline xylans were linear polysaccharides linked by β -glycosidic bonds probably in the 1-4 positions (1). When periodate oxidized xylan was hydrolyzed no D-xylose could be found in the hydrolyzate. Had a branch point existed in the xylan chain, the anhydro-D-xylose unit at which the branching occurred would not have been attacked by periodate and would have been detected after hydrolysis.

In periodate oxidation of a linear xylan three moles of formic acid should be produced; two from the reducing end and one from the nonreducing end of the chain, and it is possible to calculate a molecular weight on this basis (5). Table VI shows the amounts of formic acid produced by periodate oxidation of the crystalline xylans and the D.P.'s calculated from these results. D.P.'s calculated from viscosity measurements and reducing power determinations are also included. The D.P.'s based on formic acid production were calculated

on the assumption that the xylans were linear. Good agreement among the three independent estimates validated this assumption and indicated that the values found were probably correct.

TABLE VI
DEGREES OF POLYMERIZATION OF CRYSTALLINE XYLANS

Crystalline xylan	Formic acid produced by periodate oxidation (mole/mole)	D.P. (formic)	D.P. (viscosity)	D.P. (reducing power)
Barley	0.069	44	60	50
Wheat	0.099	30	33	28
Rye	0.120	25	30	32

Methylation of crystalline barley xylan, followed by hydrolysis, as described in the experimental section, yielded a mixture of reducing sugars having the following composition: (a) 2,3,4-trimethyl-D-xylose, 2.0%, (b) 2,3-dimethyl-D-xylose, 97.1%, (c) monomethyl-D-xylose, 0.9%. The tri- and dimethyl-D-xylose derivatives were identified chromatographically by comparison with known compounds run on the same paper. The monomethyl-D-xylose was not identified. The amount of 2,3,4-trimethyl-D-xylose corresponded to approximately 50 residues per nonreducing end group, a value in good agreement with those found by other methods (Table VI). The 2,3-dimethyl-D-xylose was derived from a long chain of D-xylose units linked 1-4 by glycosidic bonds. The small amount of monomethyl-D-xylose must have resulted either from a branch point in the xylan chain or from incomplete methylation. A constant methoxyl content of 36.8% was obtained after nine methylations of the crystalline barley xylan, a value slightly lower than the theoretical methoxyl content of 38.7% for a dimethyl xylose. Because of the difficulty of complete methylation and because of the other evidence indicating a straight chain polysaccharide, it is probable that the monomethyl-D-xylose resulted from incomplete methylation.

From the evidence obtained it was apparent that the autoclaving of straw hemicelluloses produced a mild hydrolysis, degrading the polysaccharide chain and removing L-arabinose and D-glucuronic acid as components of hydrolytic fragments. The degree of degradation depended on uronic acid content, and its progressive removal by successive autoclavings finally left a pure xylan completely resistant to further hydrolysis by water at 120°C. Removal of the single unit side chains of L-arabinose and D-glucuronic acid must have enabled the xylan chains to associate with each other and crystallize. The similar properties and behavior of the five straw hemicelluloses indicated that they all possessed the same basic structure (1) varying only in uronic acid content and chain length.

Fig. 2 shows a paper chromatogram of the soluble fragments produced by autoclaving the straw hemicelluloses. In addition to D-xylose and L-arabinose,

a series of oligosaccharides was present. An investigation of these oligosaccharides will form the subject of a further communication.

EXPERIMENTAL

Chromatographic Procedures

All chromatograms were run on strips of Whatman No. 1 filter paper, 13.4×57.0 cm. The following solvent systems were used: (a) pyridine: ethyl acetate: water—1: 2: 2 (10), (b) methyl ethyl ketone: water—2: 1 (4), (c) butanol: ethanol: water: ammonia—40: 10: 49: 1 (11). Sugars were located on the papers by spraying with aniline hydrogen phthalate (12).

Preparation of Hemicelluloses

Extractive-free, chlorite holocelluloses (2) of barley, flax, oat, rye, and wheat straws were chosen as sources of hemicelluloses. Holocellulose (30.0 gm.) was stirred for 24 hr. at room temperature with 5% aqueous sodium hydroxide (1 liter). Three extractions were made and the combined extracts, brought to pH 7.5 by acetic acid, were concentrated under diminished pressure to 750 ml. Addition of 3 volumes of ethanol precipitated crude hemicelluloses which were purified by dialysis against running distilled water for 48 hr. After reprecipitation by ethanol the hemicelluloses were dried through solvent exchange with ethanol and ether and finally by pumping to constant weight over phosphoric anhydride and paraffin at 0.05 mm. The final products were white powders containing 1–2% ash. Yields, based on holocellulose, ranged from 24–26%.

Crystallization Procedure

Dry hemicellulose (5 gm.) was made into a thick paste with water (10 ml.) and heated for four hours at 120°C . in an autoclave. Ethanol (30 ml.) was added to the cooled mixture to precipitate high molecular weight material which was removed by centrifuging and autoclaved again. This procedure was repeated until no more ethanol soluble material was produced, four autoclavings being required. The ethanol solubles were stored for later examination. The precipitated polysaccharide was dissolved by heating for 15 min. at 120°C . in sufficient water to make a 0.2% solution (18). When this solution was cooled slowly to room temperature the polysaccharide separated as microcrystals which were removed by centrifuging and dried by washing with ethanol and ether.

Determination of Constituent Sugars

Polysaccharides were hydrolyzed to constant reducing power by 2.5% sulphuric acid at 97°C . Individual sugars in the neutralized hydrolyzates were estimated by quantitative paper chromatography (7) using solvent (a). Uronic acids were estimated before hydrolysis by the method of Tracy (15).

Viscosity Measurements

Hemicelluloses and crystalline xylans were dissolved in cupriethylenediamine to give 0.5% solutions from which 0.25%, 0.125%, and 0.0625% solutions were prepared by dilution. Flow times of freshly prepared solutions

were measured in an Ostwald-Cannon-Fenske type viscometer (ASTM 100) in a water bath maintained at $25 \pm 0.02^\circ\text{C}$. Degrees of polymerization were calculated from intrinsic viscosities using the Staudinger equation with $K_m = 5 \times 10^{-4}$ (9).

Periodate Oxidation

Samples (100 mgm.) of the hemicelluloses and crystalline xylans were suspended in water (120 ml.) to which was added 30 ml. of periodic acid solution (6.9 gm. periodic acid in 120 ml. water, neutralized to methyl red indicator by sodium hydroxide). All oxidations were carried out in a dark room at 16°C . At various time intervals analyses were carried out for periodate consumption and formic acid production (6). After periodate oxidations of the crystalline xylans were complete, excess periodate was destroyed by butylene glycol. The solutions were dialyzed against running distilled water for 48 hr. and then concentrated to sirups. These sirups were hydrolyzed by heating their solutions in water (5 ml.) with Amberlite IR 120 (0.5 gm.) in a sealed tube at 110°C . for 18 hr. (16). The resin was removed by filtration and paper chromatography of the filtrate, using solvent (a), showed no sugars. Preliminary experiments showed that the hemicelluloses and crystalline xylans were completely hydrolyzed by the resin, Amberlite IR 120, under the conditions reported.

Reducing Power Determinations

Samples (20 mgm.) of the hemicelluloses and crystalline xylans were covered with water (5 ml.) and allowed to stand at 5°C . for 96 hr. until thoroughly wet. Somogyi copper reagent (5 ml.) was then added and the determination was carried out in the usual manner (14).

Methylation of Crystalline Xylan

Crystalline barley xylan (0.722 gm.) was methylated with dimethyl sulphate (7.5 ml.) and 40% aqueous sodium hydroxide (15 ml.) in an atmosphere of nitrogen. After five methylations by this procedure the sirupy product was methylated four times with Purdie's reagents (methyl iodide and silver oxide) raising the methoxyl content to 31.7%. This product was fractionally precipitated from chloroform by adding petroleum ether. The most soluble fraction (0.344 gm.) was a white powder having $\text{MeO} = 36.8\%$. This methoxyl content was not changed by three more methylations with Purdie's reagents.

Hydrolysis of Methylated Xylan

Methylated xylan (300 mgm.) was sealed in a tube with an equal weight of Amberlite IR 120 and anhydrous methanol (15 ml.). The tube was then shaken at 110°C . for 18 hr. Methanol was removed from the opened tube by evaporation and replaced by water (15 ml.). The tube was resealed and heated as before. Removal of the resin by filtration and evaporation of the filtrate left a mixture of reducing sugars. Qualitative and quantitative (8) examinations of this mixture were done by paper chromatography using authentic samples of 2,3-dimethyl-D-xylose and 2,3,4-trimethyl-D-xylose for identifications and using solvent systems (b) and (c).

Soluble Products from Autoclavings

The ethanol solubles, produced by autoclaving the hemicelluloses, were chromatographed on paper using solvent (a). The developed chromatogram is shown in Fig. 2 in the discussion section.

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ESTIMATION OF CARBOXYL, ALDEHYDE, AND KETONE GROUPS IN CHROMIUM TRIOXIDE OXYSTARCHES¹

BY A. C. ELLINGTON² AND C. B. PURVES

ABSTRACT

Under identical conditions, corn starch amylose was more readily oxidized than the amylopectin by chromium trioxide dissolved in acetic acid-acetic anhydride, which was a nonswelling system. These differences in rate nearly vanished for samples dried through solvent exchange when the oxidant was dissolved in a swelling medium, 0.2 *M* aqueous sulphuric acid. The absolute rate of oxidation, however, was greatly reduced.

Carboxyl groups in the oxystarches were satisfactorily estimated either by ion-exchange with calcium acetate or sodium bromide solutions, or by direct titration to about pH 8.5 with aqueous alkali. The samples retained chromium compounds which grossly interfered with the determination of total carbonyl groups by condensation with hydroxylamine hydrochloride; condensation with excess sodium cyanide, and estimation of the ammonia from the hydrolysis of the cyanohydrins, gave better results.

Aldehyde groups in an oxystarch containing 0.16 *M*. of carboxyl and 0.14 *M*. of carbonyl groups were selectively oxidized with chlorous acid or alkaline hypoiodite, or were selectively condensed with sodium bisulphite solution. All three estimations indicated that about one-third of the carbonyl groups were aldehydes probably occupying the sixth positions in the glucose residues. The cyanohydrin of the oxystarch, when saponified and then hydrolyzed and reduced with boiling hydriodic acid, yielded the lactone of 2-methyl-4-hydroxyhexanoic acid, the recovery of which showed that at least 17% of the carbonyl groups occurred as 2-ketoglucose residues.

INTRODUCTION

Publications regarding the action of diverse oxidizing agents on starches number well over 250, and have been reviewed in several standard books (17, 27, 36). For the most part, the literature is concerned with the preparation and physical properties of the industrially valuable "soluble" and "thin boiling" modifications of starch (dextrins) rather than with the chemistry of the oxidations. The researches dealing with chromic acid oxystarches, for example, revealed little of the chemical nature of the products beyond the facts that they contained acidic (15, 28, 39) and reducing or "alkali-labile" groups (14), were degraded, were difficult to free from chromium compounds, and sometimes yielded furfural when distilled (3, 19) with mineral acids. The supposition was that the furfural originated from glucuronic acid residues produced in the oxidation (17). Oxycelluloses, however, have been studied more intensively (38) and this background of knowledge formed the basis of the present research. A purified, commercial corn starch was used throughout, and the oxidant, chromium trioxide, was dissolved either in 0.2 *M* aqueous sulphuric acid or in acetic acid kept anhydrous by admixture with acetic anhydride. Although the oxidizing power of both solutions remained constant for many hours and was readily estimated iodometrically, the accessibility of the starch to the former was greatly increased by swelling,

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whereas the latter was a nonswelling system producing negligible oxidation in unbroken, dried starch granules (9).

DETERMINATION OF CARBOXYL AND CARBONYL GROUPS

Most of the methods for estimating carboxyl groups in acidic oxystarches depend upon ion-exchange with a soluble salt, MX.



Elizer (7) employed silver *o*-nitrophenolate or cupric acetate as the salt MX and measured the decrease in silver or cupric ion in the supernatant liquor. The silver reagent at least would probably give inaccurate results with chromium trioxide oxystarches owing to their content of chromium ash (6) and reducing groups (5). The use of sodium chloride and titration of the acid liberated in the liquor (14) was probably free from these objections, and a similar method employing 1 *N* sodium bromide (35) gave the results shown in column 4 of Table I. These results agreed within $\pm 6\%$

TABLE I
CARBOXYL CONTENT OF CHROMIUM TRIOXIDE AND CHROMIC ACID OXYSTARCHES

Sample	Milliatoms O consumed ^a	Millimoles carboxyl ^a	
		By Ca(OAc) ₂	By NaBr
<i>Oxidation with CrO₃ in acetic acid – anhydride at 21°C.</i>			
I	260	81	78
	260	85	80
II	278	90	94
	278	85	90
III	265	85	92
	265	80	90
<i>Oxidation with CrO₃ in 0.2 M sulphuric acid at 21°C.</i>			
IV	310	81	86
	310	79	84
V	570	158	162 ^b
	570	162	166 ^b

^aPer anhydroglucose unit.

^bValues by direct electrometric titration against standard alkali to pH 8.3, 159, 157 mM.

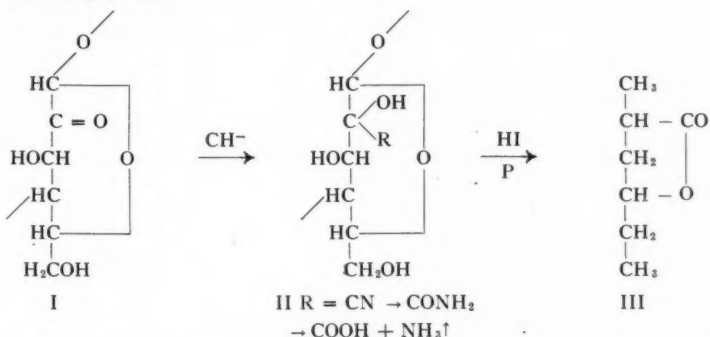
with those obtained with 0.5 *N* calcium acetate, another standard method for oxycellulose (9, 22, 23, 37, 41), and also with others based on the electrometric titration of the acidic oxystarch suspension to pH 8.3 with standard alkali. The last method required more extensive checking, because the existence of a Donnan equilibrium rendered it inapplicable to oxycelluloses (38). Fortunately Mattisson and Legendre (21) have independently confirmed the validity of a similar procedure.

Apart from the reducing power and some colorimetric tests, the estimation

of carbonyl groups in oxystarches and oxycelluloses depended on condensation to oximes with a solution of hydroxylamine hydrochloride initially near pH 5,



followed by a potentiometric titration of the hydrochloric acid liberated (9, 22, 31). This highly buffered system made the titration of low accuracy when the content of carbonyl groups was small, and the presence of adsorbed chromium compounds caused serious interference (see below). The aldehyde and ketone groups in simple sugars, however, could be estimated satisfactorily by hydrolyzing the corresponding cyanohydrins and noting the amount of ammonia produced (2). Structure II illustrates the principle of the method for the oxystarch unit I, in which the carbonyl group was arbitrarily assigned to the second position.



When the sodium cyanide solution was added to the sample at a pH of 8 or more, the suspension turned purple and then orange, although no further deepening in color occurred on standing. This evidence of degradation made it desirable to form the cyanohydrin at the lowest convenient pH. Since Head (11) found that the tetraaldehyde produced by oxidizing methyl- β -cellobioside with periodic acid changed only very slowly when kept in a buffer at pH 9.5, although rapidly in one at pH 10.5, the lower value was chosen for the present estimation. The condensation of 1-gm. samples of the oxystarch with 40 cc. volumes of 0.38 *M* sodium cyanide was carried out at 20°C., and in one case the millimoles of cyanide consumed per glucose residue were 70, 81, 86, 90, 85, and 92 after 3, 6, 9, 12, 18, and 24 hr., respectively. A time of at least 12 hr. was chosen, and the reproducibility of the estimation was assessed as $\pm 4\%$ for oxystarches in which carbonyl groups were plentiful.

If it was assumed that all of the carboxyl groups originated from primary alcohol units in the starch, each group represented the consumption of 2 atoms of available oxygen from the chromium trioxide. Table II, column 4, expresses the results of estimations with calcium acetate as a percentage of the oxidant reduced in the preparation of various oxyamyloses, oxyamylpectins, and oxystarches. Column 6 records the similar percentages recovered as carbonyl groups, each of which required only 1 atom of oxygen in its

TABLE II
 ESTIMATION OF CARBONYL GROUPS BY THE CYANOHYDRIN METHOD

Sample	Milliatoms O consumed ^a	COOH by Ca(OAc) ₂		CO by HCN		Recovery of oxidant, %	Ash, %
		mM. ^a	%	mM. ^a	%		
<i>Oxidation with CrO₃ in acetic acid - anhydride at 21°C. for 1 hr.^b</i>							
Amylose	400	113	56	118	30	86	0.3
{ Amylose	200	52	52	88	44	96	0.4
{ Amylopectin	80	35	87	14	18	105	0.6
<i>Oxidation with CrO₃ in 0.2 M sulphuric acid at 21°C.^c</i>							
Amylose	300	66	44	102	34	78	0.4
Amylose	130	34	52	62	48	100	0.2
Amylopectin	520	158	60	131	25	85	4.8
Amylopectin	300	81	54	99	33	87	2.5
Starch	580	163	56	151	26	82	5.6
Starch	540	158	58	140	26	84	—
Starch	540	160	60	138	26	86	—
Starch	400	120	60	102	26	86	—
Starch	300	81	54	92	31	85	3.1
Starch	200	60	60	68	34	94	1.2
Starch ^d	540	40	15	99	18	33	3.8

^a Per anhydroglucose unit.^b Yields 102 to 104% uncorrected for ash.^c Yields 95 to 98% uncorrected for ash.^d Recovered in 85% yield after electrodialysis.

formation. Since the total recovery of oxidant (column 7) as carboxyl plus carbonyl groups was 90% of the amount used (within a cumulative analytical error of perhaps $\pm 10\%$) and since the yield of the oxidized products was nearly quantitative, it appeared that the cyanohydrin estimation of carbonyl groups contained no gross systematic error. The recovery of only 33% of the oxidant in the last experiment noted in the table was left out of consideration, because the ash in this oxystarch had been reduced from 6% to 3.8% by electrodialysis, and the yield was only 85%. Degradation of the starch to acidic, reducing, dialyzable substances was therefore considerable during the oxidations. Concurrent estimations of carbonyl groups by the hydroxylaminehydrochloride method, made on the acidic samples and not shown in the table, were usually about 90% of the cyanohydrin value when the ash contents were 0.4% or less (column 7), but were only 30% to 60% with ash of 2.5% or more. Negative values were occasionally observed with acidic amylopectins of very high ash content.

The suggestion in Table II, lines 2 and 3, that amylopectin consumed the oxidant from acetic acid - acetic anhydride solution much more slowly than amylose was confirmed in a similar experiment employing 200 milliatoms of available oxygen per anhydroglucose unit and samples from which water had been removed by direct drying *in vacuo*. After one hour, the amylose

had consumed 195 milliatoms of the available oxygen and had acquired 45 mM. of carboxyl groups, while the corresponding figures for the amylopectin were 90 milliatoms and 39 mM. These results were not significantly altered when the samples were dried through methanol and benzene instead of directly. In more drastic oxidations, carried out for two hours with 600 milliatoms of available oxygen, the amylose consumed 400 and the amylopectin only 120 milliatoms, and the production of carboxylic acid was 113 and 40 mM., respectively. The greater reactivity of amylose in acetic acid - acetic anhydride had been previously observed by Hirst, Plant, and Wilkinson (12) during experiments on acetylation with chlorine gas as a catalyst. These differences in reactivity probably had a physical origin because they practically disappeared when samples dried through solvent-exchange were oxidized in 0.2 *M* aqueous sulphuric acid, a swelling agent. Fig. 1, Plot A, which illustrates

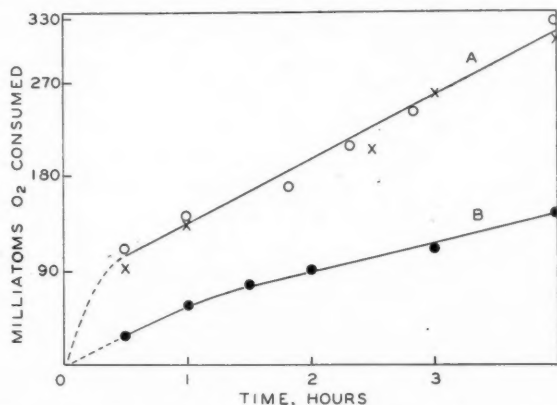


FIG. 1. Rates of oxidation in 0.2 *M* sulphuric acid with 600 milliatoms of available oxygen from chromium trioxide per glucose residue. Plot A, amylopectin, X, and amylose, O, dried through methanol-benzene. Plot B, amylose, ●, dried directly.

this point, also represents the behavior of amylopectin dried directly from water at room temperature. Amylose was peculiar in that direct drying markedly reduced its reactivity (Plot B), perhaps because it was rendered almost insoluble in water and incapable of being dispersed again. Direct drying did not have this effect on amylopectin. Felton, Farley, and Hixon (8) observed that aqueous bromine in the presence of barium carbonate oxidized a soluble "beta-amylose" fraction four times as rapidly as the corresponding "alpha-amylose". A comparison with the present result could not be made because the physical state of these fractions and their relationship to amylose and amylopectin were not specifically studied.

DIFFERENTIATION OF ALDEHYDE AND KETONE GROUPS

Although acidic sodium chlorite solution had no significant effect on unmodified starch or cellulose, or on ketose sugars, Jeanes and Isbell (16) showed that the reagent oxidized aldoses quantitatively to aldonic acids.

Reasonable results were obtained when the decrease in total carbonyl, and the increase in the carboxyl content, caused by the reoxidation of oxycelluloses with chlorous acid, was attributed to aldehyde functions (22, 23, 38). A similar reoxidation of two samples of chromium trioxide oxystarch (Table III)

TABLE III
ESTIMATIONS OF ALDEHYDE GROUPS IN STARCHES WITH ACID SODIUM CHLORITE

Reoxidation ^a	Oxystarch A		Oxystarch B	
	COOH ^b	CO ^c	COOH ^b	CO ^c
Before	162	151	89	96
After	200	110	121	64
Increase or decrease Apparent aldehyde	+38 39/151 = 26%	-41	+32 32/96 = 33%	-32

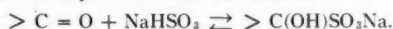
^aWith excess 4% sodium chlorite at pH 2.5 and 25°C. for one hour.

^bMillimoles per glucose unit by calcium acetate method.

^cMillimoles per glucose unit by cyanohydrin-ammonia method.

gave a quantitative recovery of the products, and the increase in carboxyl was neatly balanced by the decrease in total carbonyl content, as was expected. The inference was that 26% to 33% of the total carbonyl groups were aldehydes.

Another method of differentiating aldehydes from ketones was based on the work of Siggia and Maxcy (32), who estimated simple aldehydes by condensing them with standard bisulphite solution and titrating the excess bisulphite potentiometrically with standard alkali



Similar titrations in the presence of ketones differed in having no pronounced end point, perhaps because the above equilibrium was far to the left for ketones instead of being far to the right. Other workers (34) showed that the specific rotation of glucose, but not of fructose, was greatly changed in aqueous sodium bisulphite, while Davidson (4) observed that more bisulphite was bound by periodate oxycellulose (a dialdehyde structure) than by a dichromate oxycellulose at a comparable level of oxidation. Nevell (23) noted the combination with nitrogen dioxide oxycelluloses. The application of Siggia and Maxcy's method to two samples of oxystarch indicated that 29% to 37% of the total carbonyl content was aldehydic (Table IV). These reasonable results, however, must still be regarded as tentative.

The third method of differentiation depended upon the selective oxidation of aldoses, as opposed to ketoses, by alkaline hypoiodite (1), and the conditions chosen, pH 9.7 for two and one-half hours, were similar to those successfully used for hydrocelluloses (20, 29). Control experiments with unmodified starch were necessary. Since the hypoiodite estimated only 34% of the carbonyl groups (Table IV) found in the oxystarches by the cyanohydrin method (also at pH 9.7), it seemed likely that degradation by the alkalinity did not

TABLE IV
ESTIMATIONS OF ALDEHYDE GROUPS WITH SODIUM BISULPHITE
AND WITH ALKALINE HYPOIODITE

Method	Oxystarch C, ^a millimoles CO	Oxystarch D, ^b millimoles CO
<i>Bisulphite</i> ^c	41, 39	34, 34
Apparent aldehyde ^d %	29, 28	37, 37
<i>Hypoiodite</i> ^e	48	32
Apparent aldehyde ^d %	34	34

^aOriginally 141 mM. CO per glucose unit by cyanohydrin method.

^bOriginally 93 mM. CO.

^cExcess 1 M sodium bisulphite at pH 7.5 for three hours, then titration to pH about 9.5.

^dQuotient of 41 by 141 mM., etc.

^eSodium hypoiodite, 0.1 N, at pH 9.7 and 25°C. for two and one-half hours.

interfere seriously and that the oxidation was restricted to the original aldehyde groups. Although the gross over-oxidation reported for oxycelluloses (24) suggested that the hypoiodite method was of doubtful reliability, in the present case it supported the conclusion from the other two methods that approximately one-third of the carbonyl groups in the oxystarches were aldehydes, presumably occupying the sixth positions in the anhydroglucose units in starch. The remaining two-thirds were therefore ketone groups in the second and third positions.

DETECTION OF ANHYDRO-2-KETOGLUCOSE UNITS

If the oxystarch contained any glucose residues oxidized to ketone in the second position (Structure I), cyanohydrin followed by saponification would yield a branched chain heptonic acid unit (II, R = COOH). Complete hydrolysis of this product with constant-boiling hydriodic acid would then liberate the acid (II) with an aldehyde group in the first position, but the simultaneous reduction would change the aldehyde to a methyl unit and replace hydroxyl groups with hydrogen atoms. The product would be 2-methylhexanoic acid or its lactone (III). This was the method used by Kiliani to locate the ketone group in fructose, and the yield of the lactone (III) from this source was recently raised to about 70% of theory (26). In the same way, any 3-keto unit in oxystarch would yield 2-ethylpentanoic acid, and the product from a 6-aldehyde unit would be *n*-heptanoic acid or lactone.

The chromium trioxide oxystarch used was prepared in 0.2 M sulphuric acid, and averaged 158 mM. of carboxyl and 141 mM. of carbonyl groups per glucose unit. After the formation and saponification of the cyanohydrin, the acidic product containing (II) was isolated in nearly quantitative yield, but the carboxyl content was only 265 mM., or only 85% of the expected value of (158 + 141) 299 mM. The reason for this discrepancy was not determined. Hydrolysis with boiling 0.5 N sulphuric acid then made it possible to separate the unoxidized portion of the oxystarch as glucose, and to recover the acidic portions as barium salts in 50% yield by weight. This yield, and the barium content of 21.0% corresponded to 0.98 equivalents of barium for each carboxyl

group (0.265 M.) retained after the cyanohydrin synthesis but the analysis was not that of a single chemical individual. Hydrolysis with boiling 1 *N*, instead of 0.5 *N*, sulphuric acid reduced the yield of these salts to about 35% by weight of the original oxystarch, presumably because some of the uronic acid units were decarboxylated. The barium content of the salts, and the fact that the reducing power of the hydrolyzates increased to only 50% as glucose, suggested that most of the product consisted of difficultly hydrolyzable aldobiuronic acids.

The above barium salts were then reduced with constant-boiling hydriodic acid in the presence of red phosphorus, and the acidic portion of the product was freed from a little combined iodine by hydrogenation. After recovery, the pale yellow oil was at first methylated with diazomethane and fractionally distilled, but analyses showed the fractions to be mixtures of ester and lactone. In later experiments the oil was converted to its white barium salt, whose composition as that of a monohydroxyheptanoic acid was unchanged by reprecipitation from aqueous alcohol. This salt amounted to 13.2% by weight of the carbohydrate barium salts from which it was derived, and its barium content of 32.3% accounted for only 20% of the original carboxyl groups. Since no trace of a barium hexanoic acid was discovered, it was inferred that any remaining uronic acid residues in the oxystarch had been lost by decarboxylation during the reduction with boiling hydriodic acid. On this basis the 13.2% yield corresponded to 6% by weight of the oxystarch, or to about one-third of the 141 mM. of carbonyl groups it contained.

In a final experiment, 30 gm. of the oxystarch yielded 14 gm. of carbohydrate barium salts after cyanohydration, saponification, and hydrolysis, and the acidic oil from the reduction and deiodination was fractionally distilled at 1.5 mm. pressure. The main fraction, 0.5 gm., had the composition of a heptanoic lactone and yielded the crystalline hydrazide of 2-methyl-4-hydroxyhexanoic acid (III), the identity of which was confirmed by comparison with an authentic sample. Since 2.9 gm. of the lactone could be theoretically expected from 141 mM. of carbonyl group in the oxystarch, the observed recovery of 0.5 gm. showed that 17% of these groups were 2-keto units. This estimate was a minimum, because the recovery from pure fructose was only about 70% of theory (26), and the proper value was probably at least 25%. Aldehyde and 2-keto units therefore accounted for at least one half of the carbonyl groups in the oxystarch examined; no 3-keto units were detected, and the remaining carbonyl groups perhaps escaped identification because they were located on glucose residues oxidized in more than one way. Since the 2,3-dialdehyde structure produced by highly selective oxidants like periodic acid (38) was almost certainly absent from the oxystarch, the aldehyde units found were restricted to the 6-positions of the glucose residues.

EXPERIMENTAL

Materials

A commercial, air-dry corn starch was freed of fat by extractions with 85% aqueous methanol (30), and the amylose was isolated by dispersing 30 gm.

of the product in 1 l. of water in which 1.3 gm. of thymol and 1 gm. of sodium chloride had been dissolved (10). Yield 6.3 gm., or 21%. Stirring for one hour with 4 gm. of absorbent cotton removed traces of amylose (25) from the mother liquor, which was then concentrated under diminished pressure and diluted with 4 volumes of methanol. The precipitated amylopectin, after being dried through methanol and benzene, amounted to 23 gm., or 79%.

The whole starch employed in later experiments was extracted for one week at room temperature with 10 volumes of 97% acetic acid, and for a second week with an equal volume of fresh acid. Work carried out at the Massachusetts Institute of Technology in 1942 by our former colleague, Dr. G. E. Murray, for the Corn Industries Research Foundation, showed that this treatment removed much of the ash, fat, and nitrogen compounds, but caused no acetylation and no visible change in the starch granules. Although the product was of the thin boiling variety, the hydrolytic action of the reagent was so slight that eight days were required for a 50% hydrolysis of sucrose, and methyl- α -glucopyranoside was unaffected after six months.

Pure thiophene-free benzene freshly distilled from sodium, and methanol dried and distilled from magnesium, were used to dry the samples through solvent-exchange, and stock acetic acid was boiled under reflux with 2% of chromium trioxide to remove any reducing impurities (13). The acetic anhydride was purified by fractional distillation without adding chromium trioxide, the presence of which caused an explosion or fire.

Oxidation of the Starch Samples

(a) Thirty grams of the dried starch, defatted with 97% acetic acid, was reprecipitated with ethanol after dispersion in 1 l. of water about 70°C., and was solvent-exchanged into glacial acetic acid. Without previous drying, the product was immersed in 1 l. of a cold 4:1 mixture of glacial acetic acid and acetic anhydride containing the required amount of chromium trioxide, and the oxidation was followed iodometrically as described in the parallel work with cellulose (9). After being stirred mechanically at room temperature until an aliquot gave a negative test for the chromate ion with aqueous lead acetate, the oxystarch was recovered and was usually steeped in glacial acetic acid to remove some of the adsorbed chromic compounds. The product was freed of acetic acid *in vacuo* over solid sodium hydroxide, was washed with methanol and benzene, and was stored *in vacuo* over phosphorus pentoxide and solid sodium hydroxide.

Six-gram samples of the amylose and amylopectin were oxidized in 300 cc. volumes of the acetic acid - acetic anhydride mixture containing 0.74 gm. of chromium trioxide, an amount which afforded 0.3 atoms of available oxygen for each glucose unit. After being mechanically stirred for one hour, the products were recovered on a filter and the filtrate, plus the glacial acetic acid washings, was titrated with 0.125 *N* sodium thiosulphate in presence of excess potassium iodide to determine the oxidant consumed. The products were partially de-ashed and were isolated as already described. Attempts to remove ash with 10% instead of glacial acetic acid reduced the yield for oxyamylose

from 102% to 88% (including residual chromium ash), and of oxyamylpectin from 104% to 85%, both products being gelatinous and difficult to filter.

(b) A 60-gm. sample of the defatted starch was dispersed in 1 l. of distilled water at 80°C., and, after cooling, sufficient 20% sulphuric acid was added to make the mixture 0.2 *M*. The required amount of chromium trioxide, dissolved in 100 cc. of 2*M* sulphuric acid, was added and the mixture was stirred mechanically at room temperature until the oxidant was completely reduced. The slightly green colored product was precipitated by adding 2 volumes of methanol, was washed repeatedly in the same liquid, and was dried through benzene. Yield, 95% to 98%. An attempt to reduce the ash in a 55 gm. sample of the oxystarch by electrodialysis yielded only 47 gm. with an ash content (3.8%) that was still high. A three-compartment dialyzer with platinum electrodes operating at 110 volts and 0.5 to 0.15 amp. was used in this experiment.

Analytical Methods

The original articles described sources of error in these methods.

(a) Carboxyl groups were estimated by immersing the acidic oxystarch, 0.5 gm., in 50 cc. of 0.5 *N* calcium acetate previously adjusted to pH 8.2 (9) or in 50 cc. of 1 *N* sodium bromide (35). In each case the acid displaced in the ion-exchange was determined after 24 hr. by titration with 0.1 *N* sodium hydroxide to the pH of the blanks, and was accepted as equivalent to the carboxyl content (Table I). When this titration was carried out potentiometrically, the plot for a sodium bromide estimation practically coincided over the pH range 4 to 12 with the plot for the oxystarch suspended in distilled water, the maximum inflection occurring near pH 8.

(b) Carbonyl groups were estimated by the method just published for fructose (2). A solution of 0.3 gm. of the oxystarch in 20 cc. of 0.38 *N* sodium cyanide, buffered to pH 9.5 with aldehyde-free glacial acetic acid, was kept in a tightly stoppered vessel for 24 hr. After the addition of 8 cc. of 30% sodium hydroxide, the ammonia liberated from the hydrolysis of the cyanohydrin was quantitatively steam-distilled from a semimicro Kjeldahl apparatus into a 2% solution of boric acid containing a mixture of bromocresol green and methyl red as indicator (18). The time of distillation was standardized at 10 min., the final titration was with 0.01 *N* hydrochloric acid, and a blank determination was necessary to correct for the ammonia liberated from the excess cyanide.

(c) Aldehydes were differentiated from ketone groups by reoxidizing 6.5 gm. of the oxystarch, immersed in 145 cc. of 30% acetic acid, for one hour at pH 2.5 and 25°C. with 6 gm. of pure sodium chlorite dissolved in the minimum amount of water (22). The product was recovered by precipitation into 2 volumes of alcohol, and while in the centrifuge cup it was de-ashed by three quick extractions with a large excess of cold 70% methanol made 0.05 *N* with respect to hydrochloric acid. Any adsorbed chloride ion was thoroughly extracted with 70% methanol, and the reoxidized starch was dried through methanol and benzene. Yield 6.5 gm. or 100%. This product was then analyzed for carboxyl and carbonyl groups as described in (a) and (b).

In the second method of differentiation, 50 cc. of 1 *M* sodium sulphite, 0.5 gm. of oxystarch, and 5 cc. of 1 *M* sulphuric acid were mixed together and kept in a stoppered flask for three hours (32). Aliquots, 25 cc., were then withdrawn and titrated potentiometrically with 0.1 *N* sodium hydroxide, the break in the plot near pH 9.5 being accepted as the end point. The result, when corrected for a blank containing no oxystarch, was taken to represent the moles of aldehyde *plus* carboxyl groups, and the latter were estimated separately as described in (a).

The third differentiation involved oxidizing a 0.3 gm. sample, suspended in 30 cc. of a 0.1 *N* sodium carbonate – bicarbonate buffer at pH 9.7, with 25 cc. of 0.1 *N* iodine in 2% potassium iodide (20, 29). The oxidation was for 2.5 hr. at 25°C. Ten cubic centimeters of 0.4 *N* sulphuric acid was then added and the liberated iodine was titrated with 0.1 *N* sodium thiosulphate to a starch end point. The mixture was agitated at intervals during the titration and at the end was colorless, although some purple deposits of the starch-iodine complex remained. It was necessary to carry out a blank titration in which the addition of acid immediately followed that of the iodine to the oxystarch sample.

Preparation and Hydrolyses of Oxystarch Cyanohydrin

(a) In a typical experiment 3.0 gm. of oxystarch averaging 0.141 carbonyl and 0.158 carboxyl groups per glucose unit was mixed with 100 cc. of 0.38 *N* sodium cyanide buffered to pH 9.5 with acetic acid. After standing at room temperature for 24 hr., the orange colored colloidal solution was concentrated under reduced pressure to expel ammonia, a procedure which caused no further increase in the color. The residual liquor was neutralized with dilute hydrochloric acid and the distillation continued for another hour to remove excess hydrogen cyanide. The product was then precipitated by pouring the liquor into 5 volumes of cold methanol made 0.05 *N* with hydrochloric acid and was thoroughly washed on the centrifuge with 0.05 *N* acid in 70% aqueous methanol. Washing was continued with neutral 70% methanol until the filtrate was free of chloride ion, and drying was done through absolute methanol and benzene. Yields varied from 96% to 104%. Found: COOH by the calcium acetate method, 0.265 M. A sample, 0.5 gm., was hydrolyzed in 500 cc. of boiling *N* sulphuric acid under reflux and at 30 min. intervals the copper reducing power of the solution was estimated, as glucose, by the Shaffer-Hartmann-Somogyi (33) method. A value of about 50% of theory was reached after hydrolysis for two and one-half hours, and further increase was only very slow. The same result was attained after about five hours' hydrolysis with 0.5 *N* sulphuric acid. As previously known (40), cyanide ion had to be removed prior to these estimations.

(b) The above cyanohydration was repeated on a 10-fold scale (30 gm. of oxystarch) with the exception that sulphuric instead of hydrochloric acid was used prior to the distillation of excess hydrogen cyanide. More sulphuric acid was added to increase the normality to 0.5 *N* and the product was hydrolyzed to glucose and sugar acids by heating for five and one-half hours

under reflux on a steam bath. Two volumes of 95% ethanol were added to precipitate sodium sulphate and after its removal next day, the clear light red filtrate was freed of alcohol by distillation *in vacuo*. The residue, now 400 cc., was kept under reflux near 100°C. with barium carbonate for three or four hours, and the excess, together with barium sulphate, was removed on the centrifuge and thoroughly washed with water. Washings and filtrate, now about 2.5 l., were clarified with 8 gm. of absorbent charcoal and the clear yellow, neutral liquor was evaporated under diminished pressure to about 80 cc. and was poured into 2 volumes of 95% ethanol to precipitate the barium salts of sugar acids. After recovery next day, these salts were dissolved in the minimum amount of water, the solution was clarified with absorbent carbon, and the white salts were reprecipitated with ethanol and were dried *in vacuo* at 50°C. Yield: 14.5 gm. with a barium content of 20.8, 21.1%. A smaller-scale experiment gave a yield corresponding to 15.3 gm.

Reduction to 2-Methyl-4-hydroxyhexanoic Acid

(a) A published method was followed (26). Fourteen grams of the above barium salts, 6 gm. of red phosphorus, and 150 cc. of freshly distilled, constant boiling hydriodic acid (b.p. 127°C.) were heated together under gentle reflux for four hours. The dark mixture was cooled and extracted continuously with ether for 12 hr. to remove 14 gm. of a dark brown, acidic oil, which was recovered by evaporating the ether at atmospheric pressure. This oil was dissolved in 150 cc. of *N* sodium hydroxide, and combined iodine was reduced by high-pressure hydrogenation over 4 gm. of Raney nickel catalyst for two hours at 135°C. After recovery by extracting the strongly acidified solution with ether, 3.2 gm. of a yellow oil remained. Distillation of this product at 1.5 mm. pressure yielded 0.5 gm. of a pale yellow oil boiling at 54° to 58°C. and with a refractive index of n_D^{21} 1.4350. Found: C, 65.0, 65.4%; H, 9.5, 9.4%; neutralization equivalent 128, 129, 126.5. Calcd. for $C_7H_{12}O_2$: C, 65.6%; H, 9.4%; neut. equiv., 128. A second fraction, 0.2 gm., consisted of a thick yellow syrup distilling at 130°C. and 1 mm. pressure and with n_D^{18} 1.4680. Although crystals appeared to form in this fraction, the amount was too small to permit isolation. The more volatile fraction, 0.4 gm., when boiled under reflux for two hours with 1 cc. of hydrazine hydrate and 2 cc. of ethanol, deposited crystals which were recrystallized from chloroform. These crystals, 0.15 gm., melted at 115° to 122°C., undepressed by admixture with an authentic sample of 2-methyl-4-hydroxyhexanoic hydrazide, m.p. 123°C., kindly supplied by A. S. Perlin.

(b) Another reduction, carried out on 10 gm. of the above barium salts, yielded 2.6 gm. of the de-iodinated yellow acid oil. The crude barium salt of this oil, however, was found to contain barium iodide, which was removed by double decomposition of the aqueous solution with 3 gm. of silver sulphate. After removal of silver ion as the sulphide, careful neutralization of the filtrate with barium hydroxide, and the use of adsorbent charcoal, the liquor was evaporated to small volume. A pure barium salt, 0.85 gm., separated after several days. Found: C, 39.1, 39.3%; H, 5.9, 6.0%; Ba, 31.8, 32.0%. Calcd.

for the barium salt of a hydroxyheptanoic acid, $(C_7H_{13}O_3)_2Ba$: C, 39.5%; H, 6.1%; Ba, 31.7%. Treatment of the filtrate with 2 volumes of acetone recovered a further 0.47 gm. (Found: Ba, 32.1, 32.4%) of this salt, and increased the total yield to 1.32 gm., or to about 50 mM. per anhydroglucose unit in the original oxystarch.

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A METHOD FOR THE IDENTIFICATION OF THE MONO-*O*-METHYLGLUCOSES¹

BY R. U. LEMIEUX AND H. F. BAUER²

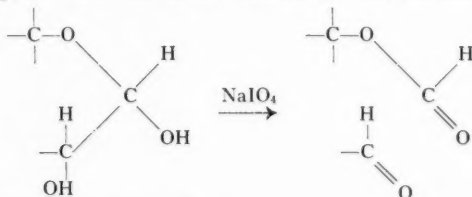
ABSTRACT

Periodate oxidation of any one mono-*O*-methylglucopyranose and alkaline hydrolysis of the product yields a substance which can be positively distinguished by paper chromatography from the products formed under the same conditions from the other mono-*O*-methylglucopyranoses. Thus, the components of a mixture of the mono-*O*-methylglucopyranoses can be readily identified. The method appears useful for the identification of di-*O*-methylglucoses. Reduction with sodium borohydride prior to periodate oxidation renders the method useful for the identification of tri-*O*-methylglucoses. The potential value of the method, which can be used on a microscale, is illustrated by an application to the characterization of the *O*-methylglucoses derived from a water-soluble *O*-methylcellulose.

A method for the identification of the components of mixtures of mono-*O*-methylglucoses was required as an aid in determining the extent and nature of acetyl group migrations during methylation with silver oxide and methyl iodide. This communication describes a method suitable for this purpose which may find useful application in studies on the composition of *O*-methylated polysaccharides.

The position-isomers for a partially *O*-methylated sugar are not usually separable by unidimensional partition paper chromatography. For example, although a mono-*O*-methylglucose fraction which contained three different mono-*O*-methylglucoses was examined (chromatogram 1, Fig. 1), no information on the chemical heterogeneity of the fraction was obtained. Although the solution to the problem could have been approached by application of two-dimensional paper chromatography, it was felt that the following method would yield more decisive information and be of more general application. The method developed involves periodate oxidation of the mixture of *O*-methylglucoses, alkaline hydrolysis of the formyl esters formed, and characterization of the products by unidimensional paper chromatography.

It is now firmly established (1, 4, 5, 12, 16) that the periodate oxidation of reducing sugars may be attended by the formation of formyl esters. The *O*-formyl groups are derived from the lactol carbon atom, as shown below, and are sufficiently stable in slightly acid media to serve as blocking groups toward further periodate oxidation. Recently, the periodate oxidation of

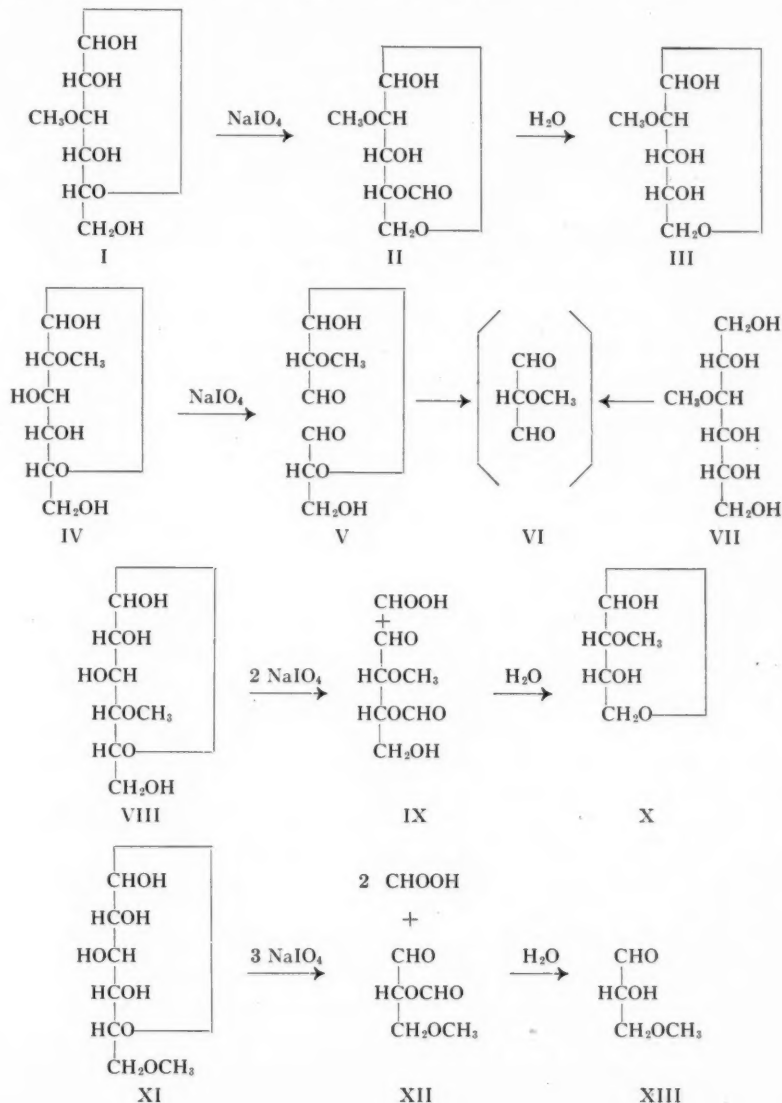


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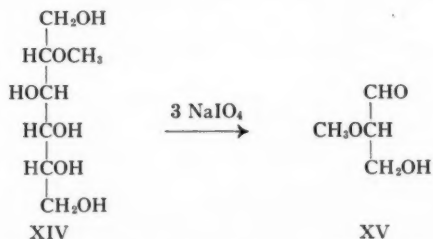
3-O-methyl-D-glucopyranose (I) has been shown (1) to yield mono-O-formyl-2-O-methyl-D-arabinose (II). It is of interest to note that the success met (3) in limiting the consumption of periodate by starch and cellulose, when the oxidation mixture is controlled within the limits of pH 2.05–4.8, to one mole of oxidant per glucose residue is in all probability related to the formation of formyl esters at the reducing ends of the polysaccharide chains.



mono-*O*-methylglucose oxidized. This appeared to be the case. However, since the formyl esters underwent hydrolysis during the chromatography, the resulting chromatograms were ill-defined. When the *O*-formyl groups were saponified prior to chromatography, the well-defined chromatograms shown in Fig. 1 were obtained.

The chromatograms shown in Fig. 1 were developed with the butanol-ethanol-water system (6) and the reducing compounds were detected with the aniline phthalate reagent (15). The periodate oxidations were carried out for one hour at 0°C. with an excess of reagent. Ethylene glycol was added to destroy the excess periodate and the solution was neutralized to phenolphthalein before application to the chromatogram. The dark spots formed at the starting point through reaction of the aniline spray reagent with the sodium iodate were not included in Fig. 1.

The main product from 2-*O*-methyl-D-glucopyranose (IV) gave a strong lemon yellow spot in the cold. Since a material was formed on periodate oxidation of 3-*O*-methylsorbitol (VII) which possessed the same R_f value (compare chromatograms 2 and 7, Fig. 1) and which gave the same color reaction, it seems likely that the substance is derived from methoxymalonaldehyde (VI). This conclusion is supported by the appearance of this spot on the chromatogram (Fig. 1, 9) for the oxidation products from the di-*O*-methylglucose fraction of the *O*-methylcellulose hydrolyzate. 2,6-Di-*O*-methyl-D-glucopyranose would also be expected to yield methoxymalonaldehyde (VI) on periodate oxidation. Attempts are being made to characterize the substance actually responsible for the color reaction. A diffuse band of greater R_f value also appeared on the chromatogram of the product from 2-*O*-methylglucose. This complication may be serious should it be desired to identify 4-*O*-methylglucose (see Fig. 1, 4) in the presence of large amounts of 2-*O*-methylglucose. 3-*O*-Methyl-D-glucopyranose (I) gave only 2-*O*-methyl-D-arabinose (III) (1). The R_f value for the product obtained from 4-*O*-methyl-D-glucopyranose is of the order expected for 2-*O*-methyl-D-erythrose (X). The product from 6-*O*-methyl-D-glucopyranose (XI) appeared to be 3-*O*-methyl-D-glyceraldehyde (XIII) since a substance of similar R_f value was obtained from 2-*O*-methylsorbitol (XIV) (compare chromatograms 5 and 6 in Fig. 1). This substance should yield 2-*O*-methyl-L-glyceraldehyde (XV). 5-*O*-Methylglucose was not tested.

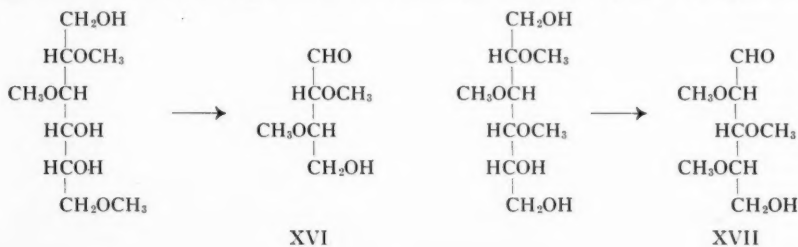


Inspection of chromatograms 2 to 5 in Fig. 1 shows that the method allows a ready and definite identification of a pure mono-*O*-methylglucose which

possesses the methyl group at positions 2, 3, 4, or 6. Furthermore, the method allows the identification of these substances in the presence of one another except, as noted above, for some interference between the 2- and 4-substituted compounds.

The potential value of the method is illustrated by the following application to the methylglucoses derived from a technical cold-water-soluble *O*-methylcellulose. The *O*-methylcellulose was completely hydrolyzed (see Fig. 1, 1) and the hydrolyzate was fractionated by means of preparative paper chromatography to yield the fractions of mono-, di-, and tri-*O*-methylglucoses. The tri-*O*-methylglucose fraction crystallized immediately to yield 2,3,6-tri-*O*-methyl-D-glucose. Application of the procedure to the mono-*O*-methylglucose fraction showed clearly the presence of the 2-, 3-, and 6-substituted glucoses. Although it could undoubtedly be accomplished, no attempt was made to put the method on a quantitative basis for analysis. Nevertheless, a comparison of chromatogram 7 with chromatograms which contained varying amounts of the products from the individual mono-*O*-methylglucoses indicated that the ratio of mono-*O*-methylglucoses was approximately 10:1:5 for the glucoses substituted at positions 2, 3, and 6, respectively. This conclusion is in agreement with the conclusions reached by several investigators (18) that, at least under certain conditions of methylation, the 2-position of cellulose is considerably more reactive than the primary position and that the 3-position is quite unreactive (11). On the basis that the 2- and 6-positions are much more reactive toward methylation than the 3-position, it must be expected that the main di-*O*-methylglucose in the *O*-methylcellulose hydrolyzate would be the 2,6-di-*O*-methylglucose. Inspection of chromatogram 9 of Fig. 1 leaves little doubt that this was the case and that only relatively small amounts of the 2,3- and 3,6-di-*O*-methylglucoses were present. Timell (19) has established analytical methods for determining the distribution of the methyl groups in a partially methylated cellulose (20).

The method should be of value as an aid in the identification of methylated sugars. For example, it could be shown in a very simple manner that the tri-*O*-methylglucose derived from the *O*-methylcellulose hydrolyzate was 2,3,6-tri-*O*-methylglucose. Only a few milligrams of material were required. The substance was unchanged by the periodate treatment (4). This result obviously eliminated 3,4,6-tri-*O*-methylglucose. The substance was reduced with sodium borohydride and the tri-*O*-methylsorbitol was subjected to the procedure. The reducing substance formed (see Fig. 1, 10) must be 2,3-di-*O*-



methyl-L-threose (XVI). 2,3,4-Tri-*O*-methyl-D-glucose would have yielded 2,3,4-tri-*O*-methyl-L-xylose (XVII) of higher R_f value and 2,4,6-tri-*O*-methyl-D-glucose would have resulted in the periodate resistant 2,4,6-tri-*O*-methyl-sorbitol.

EXPERIMENTAL

Materials

The 2-*O*-methyl- β -D-glucopyranose (10, 2), 3-*O*-methyl- α -D-glucopyranose (7, 8), and 6-*O*-methyl- α -D-glucopyranose (9) used in this work were pure crystalline compounds. Although the 4-*O*-methyl-D-glucopyranose was a sirup (14), it was prepared from pure crystalline 4-*O*-methyl-D-glucose dibenzyl mercaptal (17).

Periodate Oxidations

The *O*-methylglucose or *O*-methylglucose mixture, 1 mgm., was dissolved at 0°C. in 0.120 ml. of 0.5 *N* sodium metaperiodate solution. After one hour at 0°C., 2-3 mgm. of ethylene glycol was added and the solution was warmed to room temperature. After five minutes the solution was made alkaline to phenolphthalein by titration with 0.5 *N* sodium hydroxide solution to a stable pink end point. After five minutes, the solution, 2-30 cu.mm., was applied by means of a microburette to Whatman No. 1 paper for chromatography. The spots were kept to about 6 mm. in diameter. The same procedure was used for the *O*-methylsorbitols.

Chromatography

A descending chromatographic procedure was used with the butanol-ethanol-water system (6). Aniline phthalate solution was used as spraying reagent (15). The results obtained are summarized in Fig. 1. Table I lists the sensitivity of the color test for the products formed from the mono-*O*-methylglucoses.

TABLE I

SENSITIVITY OF THE ANILINE PHTHALATE REAGENT IN DETECTING THE PERIODATE OXIDATION PRODUCTS FROM THE MONO-*O*-METHYLGLUCOSES

Mono- <i>O</i> -methylglucose oxidized	Color of spot	Approximate R_f	Sensitivity in μ gm. of <i>O</i> -methylglucose
2-Methyl	Lemon yellow	0.22	2-3
3-Methyl	Plum	0.35	2-3
4-Methyl	Citrine	0.53	12-15
6-Methyl	Canary yellow	0.71	5-7

O-Methylsorbitols

The *O*-methylglucose, 25 mgm., and 10 mgm. of sodium borohydride were dissolved in 0.2 ml. of water. After one hour at room temperature, the excess sodium borohydride was destroyed with acetic acid and the solution was deionized in the usual manner (21). The products from the 2- and 3-mono-*O*-

methyl-D-glucoses and from the 2,3,6-tri-*O*-methyl-D-glucose were nonreducing sirups.

Hydrolysis of O-Methylcellulose

A technical *O*-methylcellulose, soluble in cold water, 26.3% methoxyl, 1.56 methyl groups per glucose residue, 1.0 gm., was dissolved in 25 ml. of concentrated hydrochloric acid, and the solution was left at room temperature for 24 hr. Water, 100 ml., was added and the clear solution was heated on the steam bath for 1.5 hr. The nearly colorless solution was evaporated *in vacuo* below 40°C. to a sirup which was dissolved in 25 ml. of water. The solution was left at room temperature overnight before the remaining hydrochloric acid was removed by passage through a column of Amberlite IR4B. Evaporation gave 1.0 gm. of colorless sirup. Chromatogram 1 of Fig. 1 shows that hydrolysis was complete.

Preparative Paper Chromatography

The *O*-methylglucoses in the above *O*-methylcellulose hydrolyzate were separated into the mono-*O*-methyl-, di-*O*-methyl-, and tri-*O*-methylglucose fractions by preparative partition chromatography (13). A 20% aqueous solution of the sirup was streaked across 47 × 57 cm. sheets of Whatman No. 3 MM paper using a mechanical device which ensured a uniform distribution over the whole length of the streak. In this way 100–120 mgm. of the sirup was applied to each sheet. The chromatograms were developed as described above. The positions of the bands were located by spraying strips cut out from each end of the sheets. The *O*-methylglucoses were extracted from the paper strips simply by stirring in water.

ACKNOWLEDGMENT

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CYCLIC METHYLENE ACETAL STABILITIES IN DIANHYDRO-HEXITOLS¹

BY SAMUEL B. BAKER²

ABSTRACT

Ring closure at the 1,4-3,6-positions in monomethylenated mannitol and iditol imparts considerable lability to the cyclic methylene acetal group. The two derivatives, 1,4-3,6-dianhydro-2,5-methylene-D-mannitol and 1,4-3,6-dianhydro-2,5-methylene-D-iditol, are easily cleaved at the 2,5-methylene positions by highly dilute acid and differ distinctly in this respect from 2,5-methylene-D-mannitol.

The cyclic methylene acetal bridge in 2,5-methylene-D-mannitol (I) is quite stable to dilute acids. The methylene bridge does not cleave unless rather drastic acid treatment is carried out. In comparison to benzylidene and ethylidene acetals and isopropylidene ketals methylene acetals are surprisingly stable. It is therefore valid to assume that the acetal ring in 2,5-methylene-D-mannitol is a low energy structure. Sterically, the mannitol carbon chain can fold in such a manner as to diminish distortion within the methylene carbon valence bonds. Benzylidene, ethylidene, and isopropylidene groups are in reality methylene groups in which one phenyl, one methyl, and two methyl groups replace hydrogen atoms respectively. Folding of the carbon chain may be more difficult, owing to steric forces, so that the inherent energy may be large enough to make benzylidene, ethylidene, and isopropylidene acetals act in a normal manner, that is, they are unstable in acidic solution.

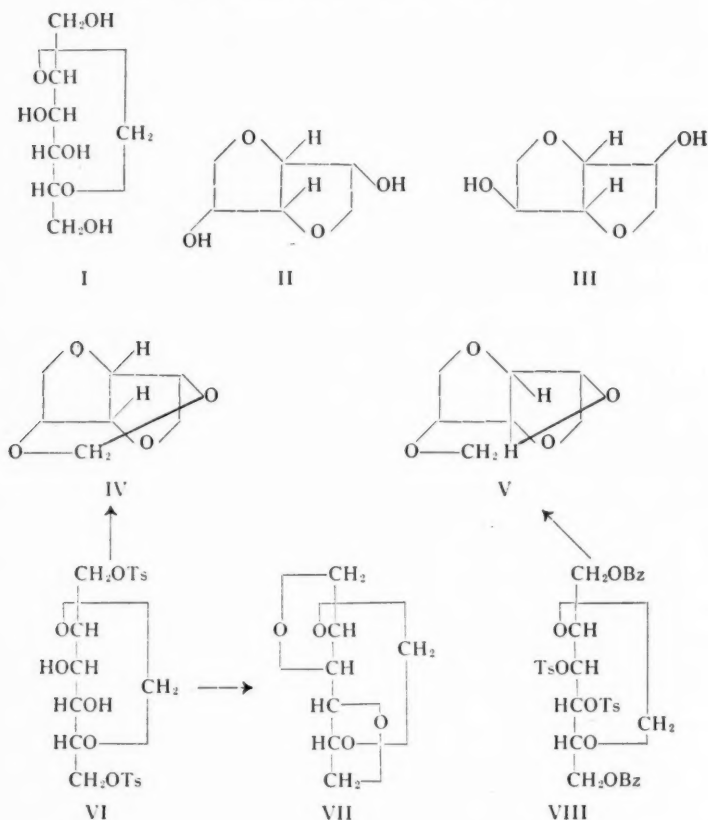
Mannitol and iditol readily form fused tetrahydrofuran rings as shown by the formation of 1,4-3,6-dianhydro-D-mannitol (II) (1, 4) and 1,4-3,6-dianhydro-L-iditol (III) (2, 6). These dianhydrohexitols (II) and (III) have been prepared by the above-mentioned authors by means of simple acid-catalyzed dehydration of D-mannitol and L-iditol respectively. The 1,4-3,6-dianhydro rings in the mannitol (II) and iditol (III) derivatives are fused tetrahydrofuran systems that are *cis*-oriented, thus imparting considerable stability to the two substances, (II) and (III).

A methylene acetal bridge across C-2 and C-5 in (II) and (III) should be under considerable strain inasmuch as the valence bond angular distortion cannot be diminished by folding of the rigid tetrahydrofuran ring structures. 1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (IV) and 1,4-3,6-dianhydro-2,5-methylene-D-iditol (V) were synthesized to compare the stability of the methylene acetals in the latter two dianhydrohexitols, (IV) and (V), to the identical group in 2,5-methylene-D-mannitol (I). The mannitol derivative (IV) proved to be very labile to 0.001 *N* hydrochloric acid and even to hot water. The iditol derivative (V) required somewhat more drastic treatment to cleave the acetal ring. Hot water had no effect whatsoever and 0.01 *N*, but not 0.001 *N*, hydrochloric acid cleaved the acetal ring in a few minutes. Although

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Bz = Benzoyl
Ts = *p*-Toluenesulphonyl

the iditol derivative (V) was less labile than the mannitol derivative (IV), both were extremely labile when compared to 2,5-methylene-D-mannitol (I).

Saponification of 2,5-methylene-1,6-ditosyl-D-mannitol (VI) with alcoholic potassium hydroxide or sodium methoxide solution yielded a dianhydromethylene hexitol. It is now generally accepted that detosyloxylation followed by ring closure occurs through the transitory formation of a carbonium cation. Ring closure occurs when the transitory carbonium cation has a hydroxyl or presumptive hydroxyl group in a *trans* position and the ring closes on the side of the molecule where the reacting hydroxyl group is situated. Therefore the dianhydromethylene hexitol can be formulated either 1,4:3,6-dianhydro-2,5-methylene-D-mannitol (IV) or 1,3:4,6-dianhydro-2,5-methylene-D-mannitol (VII). The latter structure can be dismissed on steric grounds. Removal of the methylene group with either hot water or 0.001 *N* hydrochloric acid yielded a product identical with the known isomannide. It is unlikely

that a methylene acetal group can shift under the experimental conditions used to prepare the dianhydromethylene mannitol. This is therefore further unequivocal proof of the 1,4-3,6-dianhydro-D-mannitol (II) structure for isomannide.

The iditol derivative was prepared by sodium methoxide saponification of 1,6-dibenzoyl-2,5-methylene-3,5-ditosyl-D-mannitol (VIII). Again, for the same reasons as above, it is only possible to formulate the hexitol derivative as 1,4-3,6-dianhydro-2,5-methylene-D-iditol (V). Removal of the methylene acetal with 0.01 *N* hydrochloric acid yielded a product that was identical with the known isoidide. This then is additional proof for the 1,4-3,6-dianhydro ring structure for isoidide.

EXPERIMENTAL

2,5-Methylene-1,6-ditosyl-D-mannitol (VI)

2,5-Methylene-D-mannitol (5) (50 gm.) was dissolved in hot pyridine (500 cc.). The solution was cooled (0°C.) and *p*-toluenesulphonyl chloride (100 gm.), dissolved in pyridine (200 cc.), was added over a period of 30 min. with stirring. The reaction mixture was then allowed to stand overnight at room temperature and was finally concentrated *in vacuo* to remove most of the pyridine. The remaining sirupy mass was suspended in a large volume of cold water and the sirup soon crystallized. It was filtered, washed well with cold water, and air-dried. The crude product was recrystallized once from methanol after decolorizing with charcoal. An additional recrystallization gave 94 gm. (73%) of a pure product melting at 148–149°C. and rotating $(\alpha)_D^{20} - 22.8^\circ$. These constants agreed with those found by Haskins, Hann, and Hudson (3).

A sample of the above (3 gm.) was dissolved in pyridine (20 cc.), *p*-toluenesulphonyl chloride (2.4 gm.) was added, and the solution allowed to stand 72 hr. at 40°C. The reaction mixture was cooled to 20°C. and then added to a large volume of cold water. The product separated as an oil and it slowly solidified. After the solid had been allowed to stand overnight it was broken up, filtered, and washed with cold water. The air-dried material was recrystallized from 99% ethanol and after desiccation it weighed 3.3 gm. (68%) and melted at 176–177°C. A mixed melting point determination with authentic 2,5-methylene-1-3,4,6-tetratosyl-D-mannitol was not depressed.

1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (IV)

Sodium Methoxide Method

2,5-Methylene-1,6-ditosyl-D-mannitol (20 gm.) was dissolved in chloroform (200 cc.). A sodium methoxide solution (50 cc.) containing 1.9 gm. sodium was added and, within one minute, a gel formed. The gel was soon replaced by glistening crystals of sodium *p*-toluenesulphonate. The small excess of sodium methoxide was converted to sodium carbonate by means of carbon dioxide and the separated salts removed by filtration. The slightly colored filtrate was concentrated *in vacuo* and the gummy residue mixed with hot chloroform (100 cc.). The turbid solution was filtered and the solvent

again removed *in vacuo* at 30°C. The solid residue was dissolved in hot ether (300 cc.) and the ethereal solution was decolorized with charcoal, then filtered. The filtrate was concentrated to one-half volume and cooled to -20°C. Long needlelike crystals separated in a yield of 5 gm. (80%). They were recrystallized twice more when the melting point of 84-85°C. became constant and the rotation was $(\alpha)_D^{24^\circ}$ 133.7° (CHCl₃; *c*, 10.4304; 1, 2).

Potassium Hydroxide Method

2,5-Methylene-1,6-ditosyl-D-mannitol (20 gm.) was dissolved in ethanolic potassium hydroxide (5.3 gm. in 250 cc.). The highly alkaline reaction mixture became neutral to phenolphthalein on heating under reflux. Heating was continued an additional 30 min. and the mixture was then concentrated *in vacuo* at 30°C. The gummy mass was thinned with chloroform (300 cc.) and the mixture filtered to remove potassium *p*-toluenesulphonate in quantitative yield. The chloroform solution was then concentrated *in vacuo* and the residual solid dissolved in hot ether (300 cc.) and the latter solution decolorized with activated charcoal. The solution, after filtration, was concentrated to one-half volume and on cooling to -20°C. needlelike crystals separated in a yield of 5.6 gm. (90%). An additional recrystallization from ether gave a pure product melting at 84-85°C. and rotating $(\alpha)_D^{24^\circ}$ 133.2° (CHCl₃; *c*, 8.631; 1, 2). A mixed melting point determination with a sample of the substance obtained by the sodium methoxide method, above, was not depressed.

Anal. Calc. for C₇H₁₀O₄; C, 53.16; H, 6.33. Found: C, 53.09; H, 6.46.

Methylenation of 1,4-3,6-Dianhydro-D-mannitol (II)

1,4-3,6-Dianhydro-D-mannitol (4 gm.) was dissolved in anhydrous dioxane (175 cc.) containing paraldehyde (5 gm.) and anhydrous calcium sulphate (20 gm.). The mixture was heated in a sealed bomb tube in a steam bath for 10 hr. The tube was cooled to 20°C. and the contents removed in the fume cabinet. Chloroform (380 cc.) was added and the mixture filtered. The filter was washed with a little chloroform and the combined filtrates concentrated to dryness *in vacuo*. A sirup resulted which was partially soluble in ether and it was therefore heated under reflux with anhydrous ether (300 cc.) for one hour. The ethereal solution was decanted from the undissolved sirup and the latter was triturated with a little ethyl acetate. The sirup crystallized immediately and after one recrystallization from ethyl acetate it weighed 2 gm. (50% recovery) and melted at 87-88°C. A mixed melting point determination with authentic 1,4-3,6-dianhydro-D-mannitol was not depressed.

The ethereal solution, above, was concentrated to about 75 cc. and filtered from a faint turbidity. The clear, colorless solution was cooled to -20°C. and crystals which separated in a yield of 1.2 gm. (27%) melted at 84-85°C. A mixed melting point determination with 1,4-3,6-dianhydro-2,5-methylene-D-mannitol obtained above was not depressed.

Acetolysis of 1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (IV)

1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (1 gm.) was added to an acetolyzing (5) mixture (5 cc.) at 0°C. The solid dissolved immediately and

the solution was allowed to stand 18 hr. at 5°C. The reaction mixture was added slowly with stirring to an excess of cold (5°C.) saturated potassium bicarbonate solution. The aqueous solution was then concentrated to dryness *in vacuo* at 15°C. The dry residue was extracted with warm chloroform (100 cc.) and after filtration, the solvent was removed *in vacuo*. The remaining colorless sirup was distilled at 130–133°C. at 0.08 mm. and gave 0.9 gm. of a viscous sirup. This yield was equivalent to 64% based on 2,5-diacetyl-1,4-3,6-dianhydro-D-mannitol. The specific rotation was $(\alpha)_D^{25} 119.8^\circ$ (CHCl_3 ; c , 1.602; 1, 2) and refractive index $n_D^{25} 1.4840$. A few drops of the product when heated with dilute hydrochloric acid did not give a test for formaldehyde, signifying that the methylene acetal was cleaved by the acetolyzing mixture.

The presumed 2,5-diacetyl-1,4-3,6-dianhydro-D-mannitol (0.6 gm.) was dissolved in chloroform (25 cc.). Sodium methoxide solution (5 cc. of 0.01 *N*) was added and the solution allowed to stand overnight at 5°C. Carbon dioxide gas was passed in and the mixture was then concentrated *in vacuo*. The dry residue was heated with a small volume of ethyl acetate. The latter solution was concentrated to one-half volume and after cooling to -10°C . the concentrate was inoculated with a crystal of 1,4-3,6-dianhydro-D-mannitol. Immediate crystallization occurred and the product was recrystallized once more from ethyl acetate yielding 0.39 gm. (77%) and melting at 87.5–88°C. A mixed melting point determination with authentic 1,4-3,6-dianhydro-D-mannitol was not depressed.

Effect of Hot Water on 1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (IV)

1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (1 gm.) was dissolved in distilled water (25 cc.) and the solution was distilled slowly through a 150 mm. glass column. The distillate was collected in an excess of ice-cold 2,4-dinitrophenylhydrazine hydrochloride solution. Immediate precipitation of formaldehyde-2,4-dinitrophenylhydrazone occurred and distillation was continued until 15 cc. distillate was collected. The water was replaced and distillation continued. This process was repeated six times so that practically all the formaldehyde was removed. The voluminous 2,4-dinitrophenylhydrazone was filtered, washed with a little water, and air-dried. The yield was 1.2 gm. (89%) and the melting and mixed melting points with an authentic sample were 164–167°C.

The above was repeated but the distillate was added to an excess of 5,5-dimethyl-1,3-cyclohexanedione. The dimethone of formaldehyde separated in nearly quantitative yield and melted at 187–189°C. A mixed melting point determination with an authentic sample showed 188–189°C.

The residues in both distilling flasks were combined and concentrated to dryness *in vacuo* and the gummy product dissolved in a small volume of hot ethyl acetate. The slightly colored solution was decolorized with charcoal, filtered, and then allowed to cool. The crystalline product that separated was removed by filtration and it was recrystallized once more giving 1.3 gm. (77%) melting at 87–88°C. This proved to be 1,4-3,6-dianhydro-D-mannitol as determined by a mixed melting point.

1,4-3,6-Dianhydro-2,5-dibenzoyl-D-mannitol

1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (IV) (2 gm.) was dissolved in 0.001 *N* hydrochloric acid (75 cc.) and the solution distilled *in vacuo* at 50°C. The sirupy residue was dried by distilling ethanol from it. This was repeated four times. The partially crystalline mass was then dissolved in anhydrous pyridine (25 cc.), the solution cooled to 0°C., and benzoyl chloride (4 cc.) was added. The reaction mixture was allowed to stand for two hours at 24°C., then concentrated *in vacuo*. The remaining sirup was mixed with cold water and after it had been allowed to stand overnight at 5°C. the sirup solidified. The air-dried material was dissolved in about 20 cc. ethanol and the solution decolorized with charcoal. The solution was cooled and crystallization occurred. Two additional recrystallizations from ethanol raised the melting point to 131–132°C. and rotation to $(\alpha)_D^{24^\circ}$ 224.8° (CHCl_3 ; *c*, 0.6649; 1, 2). Fletcher and Goepp (2) report m.p. 132.0–132.4°C. and $(\alpha)_D^{20^\circ}$ 225.7° (CHCl_3).

1,6-Dibenzoyl-2,5-methylene-3,4-ditosyl-D-mannitol (VIII)

1,6-Dibenzoyl-2,5-methylene-D-mannitol (5) (25.2 gm.) was dissolved in anhydrous pyridine (90 cc.). The solution was cooled to 0°C. and *p*-toluenesulphonyl chloride (26.4 gm.) was added. The reaction mixture was allowed to stand for three days at 40°C. and then concentrated *in vacuo* to remove most of the pyridine. The dark-brown residue was mixed with a large volume of cold water and the sirup soon solidified. The solid mass was broken up, filtered, and washed with cold water. The air-dried crude material was recrystallized from methanol yielding perfect hexagonal plates. The partially purified material was recrystallized once more from the same solvent and the yield was 40.6 gm. (91%). It melted at 112–113°C. and rotated $(\alpha)_D^{24^\circ}$ 13.7° (CHCl_3 ; 1, 2; *c*, 7.2828).

Anal. Calc. for $\text{C}_{35}\text{H}_{34}\text{S}_2\text{O}_{12}$; C, 59.15; H, 4.78; S, 9.01. Found: C, 59.21; H, 4.83; S, 9.0.

1,4-3,6-Dianhydro-2,5-methylene-D-iditol (V)

1,6-Dibenzoyl-2,5-methylene-3,4-ditosyl-D-mannitol (VIII) (27.3 gm.) was dissolved in dry chloroform (200 cc.). Sodium metal (1.8 gm.) was dissolved in methanol (65 cc.) and the solution was added to the chloroform solution. The mixture was allowed to stand at room temperature (24°C.) for 24 hr. The slight excess of sodium methoxide was converted to carbonate with carbon dioxide gas and the mixture filtered to remove the sodium salts. The filtrate was concentrated *in vacuo* at 40°C., the residue was dissolved in chloroform (100 cc.), and the solution treated with decolorizing charcoal to remove a trace of color and turbidity. The colorless sirup that remained after solvent removal was dissolved in a little ethyl acetate and crystallization occurred after several hours' standing at room temperature. The crystalline mass was recrystallized from ethyl acetate and it weighed 4.6 gm. (76%), melted at 83–84°C., and rotated $(\alpha)_D^{22^\circ}$ -152.1° (CHCl_3 ; 1, 2; *c*, 0.4108). Mixed melting point determinations with 1,4-3,6-dianhydro-2,5-methylene-D-mannitol and with isomannide were depressed over 20°C.

Anal. Calc. for $\text{C}_7\text{H}_{10}\text{O}_4$; C, 53.16; H, 6.33. Found: C, 53.11; H, 6.41.

Effect of Hot Water on 1,4-3,6-Dianhydro-2,5-methylene-D-iditol (V)

The above (V) (0.5 gm.) was heated under reflux for two hours with distilled water (50 cc.) in a stream of nitrogen. The gas was passed through cold (5°C.) water (250 cc.). Formaldehyde could not be detected. The water was then removed from the reaction mixture *in vacuo* at 50°C. and the sirup, after drying with ethanol, was dissolved in a small volume of ethyl acetate. The solution was seeded and after two hours, crystals of 1,4-3,6-dianhydro-2,5-methylene-D-iditol (V) separated as shown by a mixed melting point determination with an authentic sample.

Effect of Dilute Hydrochloric Acid on 1,4-3,6-Dianhydro-2,5-methylene-D-iditol (V)

The above (V) (0.5 gm.) was dissolved in 0.001 *N* hydrochloric acid (50 cc.). A stream of nitrogen was passed through the solution, while it was heated under reflux for 30 min. The gas was passed into cold (5°C.) water (250 cc.). A test for formaldehyde was negative. The solution was then taken up with more hydrochloric acid to give a normality of 0.01 *N* and heating continued. Formaldehyde was detected after 10 min. by means of 2,4-dinitrophenylhydrazine hydrochloride. The acidic solution was then concentrated *in vacuo* at 50°C. and the remaining colorless sirup was dried by distilling ethanol from it. The dried sirup was dissolved in a small volume of ethyl acetate and allowed to stand overnight at 22°C. after which tufts of crystals separated. After filtration and desiccation the yield was 0.18 gm. (40%) and the product melted at 63–64°C. A mixed melting point determination with authentic 1,4-3,6-dianhydro-D-iditol was not depressed.

1,4-3,6-Dianhydro-2,5-dibenzoyl-D-iditol

The filtrate from the above isolation of 1,4-3,6-dianhydro-D-iditol was concentrated *in vacuo* and the resulting sirup (0.23 gm.) dissolved in anhydrous pyridine (4 cc.). The solution was cooled to 0°C. and benzoyl chloride (0.5 cc.) was added. The reaction mixture was allowed to stand overnight at 22°C., then poured into cold water (50 cc.). Cold saturated potassium bicarbonate solution was added to dissolve benzoic acid and the sirup solidified after standing for three days at 5°C. The solid was broken up, filtered, and washed. It was dried in air and recrystallized twice from butanol-1. The yield was 0.34 gm. and the product melted at 110–111° and rotated $(\alpha)_D^{25} -140.6^\circ$ (CHCl₃; 1, 2; *c*, 0.7724). The reported (1) constants for the enantiomorph are m.p. 111.0–111.3°C. and $(\alpha)_D^{25} 141.9^\circ$ (CHCl₃).

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THE FLOW PROPERTIES AND MESOMORPHIC BEHAVIOR OF ANHYDROUS SOAPS AT ELEVATED TEMPERATURES

PART I. SODIUM STEARATE ABOVE 200°¹

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ABSTRACT

Although there is a large body of literature dealing with the transition temperatures of the alkali metal salts of the fatty acids, it has not always been possible to feel confidence in their graphical determination. Hitherto few measurements have been made of the viscosity of soaps as a function of temperature and rate of shear, though such measurements promise to prove useful, as sharp changes have been observed in the regions of previously reported transition points. The viscosity apparatus is described and the results obtained with anhydrous sodium stearate given, from the aspect of transition temperatures and as a study of flow properties.

INTRODUCTION

Fatty acid soaps belong to that interesting class of compounds which exhibit mesomorphism, first observed in 1888 by Reinitzer (4), and on heating pass through a series of transitions before melting to isotropic liquids. Though the intermediate phases have sometimes been described as liquid crystalline, the term is probably not a good one, since these phases have the properties of true liquids with the ability to flow.

The conditions favorable to the formation of mesomorphic phases, given by Bernal and Crowfoot (1), are these.

- (a) The molecule should be geometrically anisotropic.
- (b) The molecule should contain only one strongly polar group, though weakly polar groups may also be present.

That the alkali metal salts of the fatty acids are mesomorphic is therefore not surprising.

The transitions manifest themselves by sharp changes in appearance, most conspicuous when seen between crossed nicols in the polarizing microscope, in electrical conductivity, density, thermal capacity, and, as will be shown below, in viscosity, as the temperature varies.

The evaluation of a transition point is dependent upon plotting the property under observation against temperature and determining by inspection the position of a change in slope. This is a difficult thing to do accurately and objectively, especially where large changes do not occur. Some transition temperatures appear to have been assigned on rather meager evidence when a single property is being considered and therefore there is not complete agreement in the interpretation of results. For instance, using the dilatometer, some authors (8) found transitions at 90° and 117°, whereas others did not (6). Table I contains transition temperatures collected from published work.

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TABLE I
REPORTED TRANSITION TEMPERATURES OF ANHYDROUS SODIUM STEARATE

Name of transition	Calorimetric (9) <i>g</i>	Electrical conductivity (10) <i>h</i>	Dilatometer		Viscosity (5) <i>k</i>	Hot wire	
			Vold (8) <i>i</i>	Stainsby (6) <i>j</i>		Vold (7) <i>l</i>	Vold (8) <i>m</i>
A. Curd to supercurd	70	<i>b</i>	<i>a</i>	<i>a</i>	65	<i>a</i>	<i>a</i>
B. Supercurd to subwaxy	93	<i>b</i>	90	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
C. Subwaxy to waxy	116	<i>b</i>	117	<i>a</i>	110	<i>a</i>	<i>a</i>
D. Waxy to superwaxy	132	<i>b</i>	132	135	125	132	130
E. Superwaxy to subneat	<i>d</i>	<i>b</i>	167	<i>a</i>	<i>b</i>	167	166
F. Subneat to neat	209	<i>b</i>	198	199	<i>b</i>	203	205
G. Melting point	226	255	257	262	<i>b</i>	257	260
	<i>b</i>	278	288 <i>e</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>c</i>

Notes:

- a. No transition observed.
- b. No observation made.
- c. Not clear from paper whether *a* or *b*.
- d. Too small to be observed. Vold's sample II data (9).
- e. Confirmed visually (8).
Named transitions have been observed visually.

References in literature cited:

- g. Table I in Vold (9).
- h. Table II in Vold and Heldman (10).
- i. Table I in Vold, Macomber, and Vold (8).
- j. From Fig. 2 in Stainsby, Farnand, and Puddington (6).
- k. From Fig. 3 in Southam and Puddington (5).
- l. Table I in Vold (7).
- m. Table II in Vold, Macomber, and Vold (8).

Since previous work (5) had indicated that the viscous behavior of anhydrous sodium stearate is quite sensitive to phase transition at lower temperatures, it was decided to study this property in the higher temperature region to determine whether it had advantages over methods previously employed in indicating transitions and could contribute useful information as to the nature of the changes that occur in soap as it is heated to the temperature where isotropic liquid is formed.

EXPERIMENTAL

To determine the viscosity of sodium stearate in the range 285° to 336° a modified Poiseuille method was used with an apparatus constructed from Pyrex glass. Calculation showed that under the conditions of the experiments the correction sometimes necessary for the kinetic energy of the liquid leaving the capillary section was negligible. The Couette correction was also small, since the measured viscosity of a mineral oil* agreed well with the known value of 6.95 poises, as will be seen in Table II.

A diagram of cell III is shown in Fig. 1. While this differed slightly in the design of the end bulbs from cells I and II, it is representative of the apparatus used. The cell was filled with powdered sodium stearate between *A* and *A'*, placed in an inverted position (i.e., side tubes *CA* and *A'C'* above the capillary section) in an electric furnace (25 cm. long and 7 cm. diameter, internal) and heated to 320° under a hard vacuum. Thereby, the soap is rendered anhydrous

*Kindly supplied by Imperial Oil Limited.

TABLE II
 CELL DIMENSIONS

	Length, cm.	Radius, cm.	Viscosity of oil, poises
Cell I	8.9	0.0521	*
Cell II	10.0	0.0848	7.12
Cell III	10.5	0.102	6.92
Cell A	3.3071	0.0824	—
Cell B	2.6111	0.03683	—

*No determination.

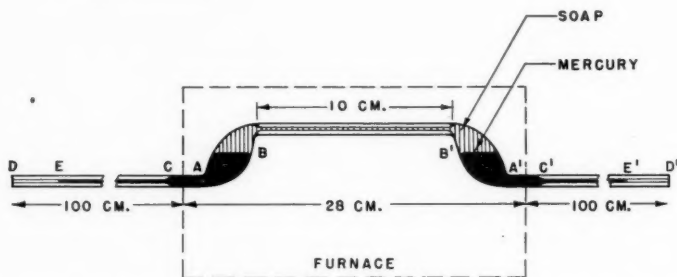


FIG. 1. Cell III in "normal" position with index tubes attached at C and C'. Not to scale.

(6). The furnace was allowed to cool to room temperature and the soap solidified, filling the cell, which was then restored to its normal position. Meter lengths of capillary tubing *DC* and *C'D'* were sealed on to the cell at *C* and *C'* and well-boiled mercury distilled in under vacuum (10^{-5} mm.) until the apparatus was filled from *E* to *B* and *B'* to *E'*. The furnace temperature was again raised to the required value, giving a volume of liquid sodium stearate, free and isolated from air and water. This was caused to flow by applying nitrogen under pressure from a cylinder to *D* or *D'*, at a rate which could be calculated from the observed movement of the end of the mercury thread in the index tubes, and the pressure was read from a mercury manometer. Before making determinations of the rate of flow as a function of the pressure, the furnace was allowed a day in which to come to thermal equilibrium. The pressure required to overcome the viscous resistance of the mercury ($\eta = 0.015$ poises) in the index tubes, which are at room temperature, is so small in comparison with that required to cause the flow of the soap that it can be neglected.

The glass apparatus was not considered safe at temperatures below 280° , because of the pressures involved, and an extrusion viscometer (3) was brought into use: a steel cylinder 18 cm. in length and 2.5 cm. internal diameter carried a pressure fitting at its upper end and one of the two interchangeable capillary tubes at its lower end. In Table II are given the dimensions of the capillaries; the apparatus when set up with the wider capillary is called cell *A* and with the narrower, cell *B*. The pressure fitting con-

nected via a manifold and a 10 liter ballast vessel to a nitrogen cylinder and calibrated gauges on the manifold, and a mercury manometer, connected to it, enabled accurate measurement of pressure to be made. An automatically controlled furnace in which the cylinder was mounted gave temperatures constant to $\pm 0.5^\circ\text{C}$.

The apparatus was flushed with nitrogen, and dry sodium stearate put into the cylinder and well shaken down; after which the piston, 1 cm. in depth, was inserted and the pressure fitting replaced. Following further flushing with nitrogen the temperature was raised to the required value.

When the temperature had been steady for an hour, the sodium stearate was extruded at different rates, by varying the pressure, and collected in weighing bottles. At a given temperature and pressure several samples were taken to secure an accurate determination of the rate of flow and to demonstrate that it was independent of time.

The lower limit of usefulness of the apparatus was about 210° ; when the viscosity of the sodium stearate becomes high, about 10^5 poises, and the nitrogen forces its way between the piston and the cylinder walls, forming channels through the soap and escaping from the capillary.

The soap used in the experiments was prepared by titration from stearic acid having a melting point of 68° – 69°C .

RESULTS

Rate of flow against pressure applied is plotted in Figs. 2, 3, 4, and 5, for cell I, cell II, cell III, and cell A* respectively, and the units of rate of flow are cubic centimeters per second, excepting in Fig. 5 where they are grams per second; and of pressure, dynes per square centimeter.

The apparent viscosity, calculated from Poiseuille's equation, is plotted as a function of inverse rate of flow in Figs. 6, 7, and 8 for cell II, cell III, and cell A,* respectively.

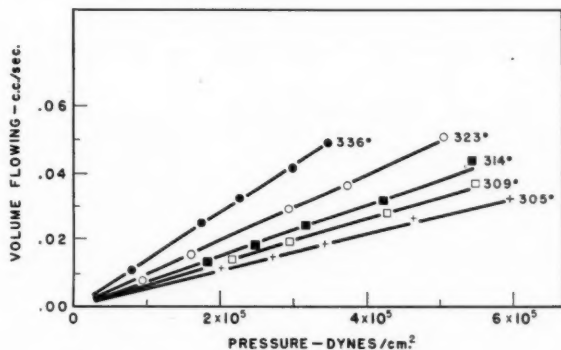


FIG. 2. Rate of flow - pressure curve. Anhydrous sodium stearate in cell I.

*Results for cell B were similar and are not shown.

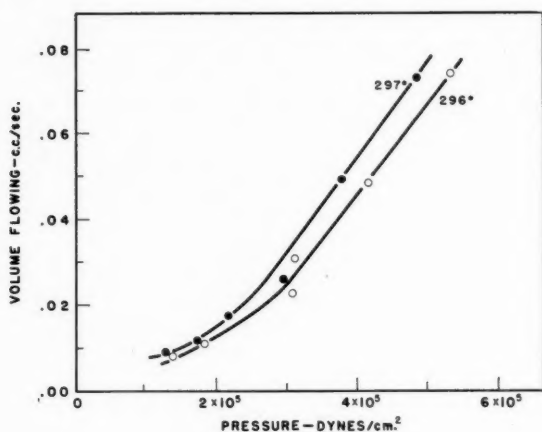


FIG. 3. Rate of flow-pressure curve. Anhydrous sodium stearate in cell II.

FIG. 4. Rate of flow-pressure curve. Anhydrous sodium stearate in cell III.

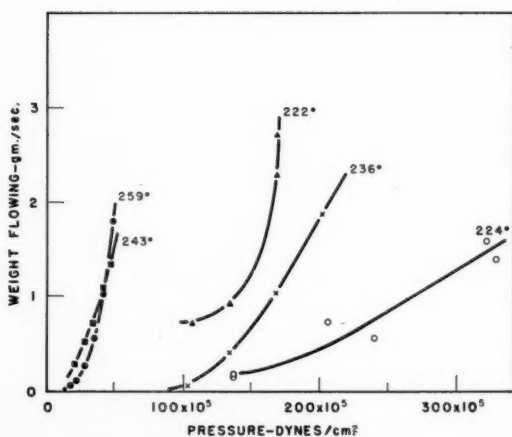
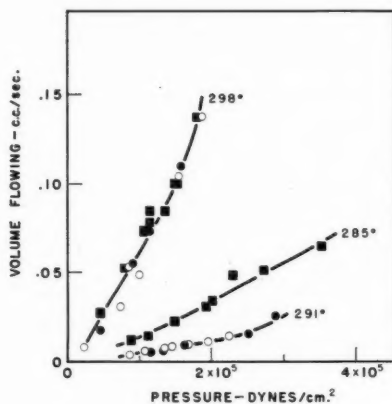


FIG. 5. Rate of flow-pressure curve. Anhydrous sodium stearate in cell A. Ordinate for 224° curve shown $\times 10^{-1}$.

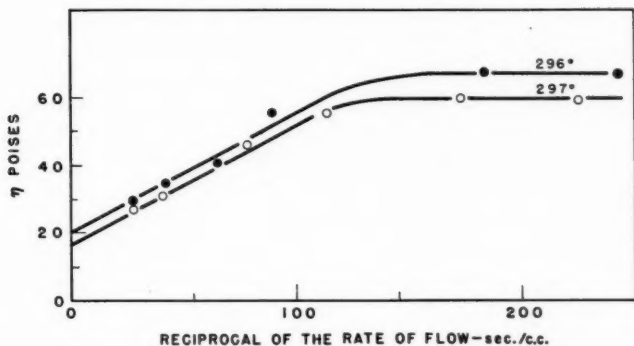


FIG. 6. Apparent viscosity - reciprocal rate of flow curve. Anhydrous sodium stearate in cell II.

The viscosity above 305° , as determined by cell I, is independent of the rate of flow, unlike that at lower temperatures, and the plot of viscosity against reciprocal rate of flow is a straight line of zero slope and is accordingly not reproduced.

In Fig. 9, viscosity at infinite rate of shear, as read by extrapolation from Figs. 6, 7, and 8, is plotted against temperature.

DISCUSSION

At temperatures above 305° the volume of sodium stearate flowing per second is directly proportional to the pressure, giving a straight line consistency curve which passes through the origin (Fig. 2), demonstrating that the flow is that of a Newtonian liquid. Knowing the constants of the viscosity apparatus, the slope of the pressure - rate of flow curve, and using the Poiseuille equation, the viscosity of sodium stearate is readily calculated and it is seen from Fig. 9 to decrease gradually with rise of temperature.

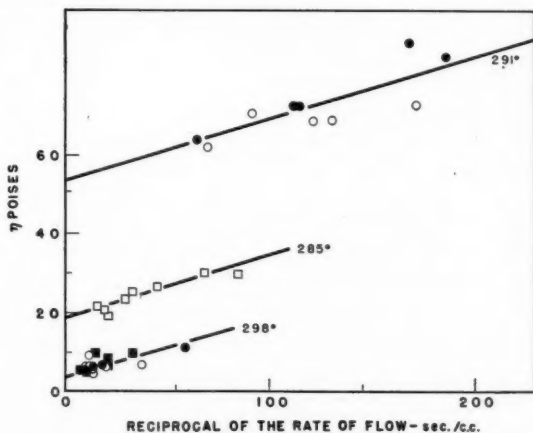


FIG. 7. Apparent viscosity - reciprocal rate of flow curve. Anhydrous sodium stearate in cell III.

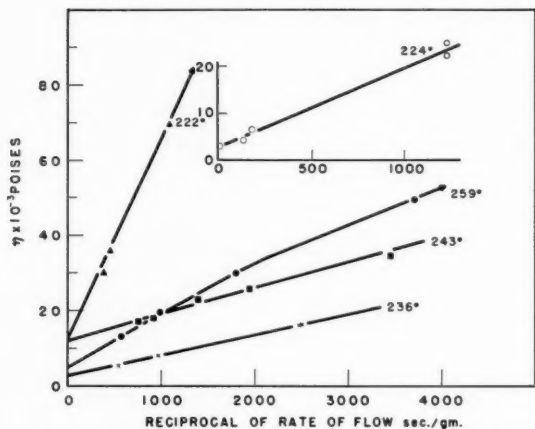


FIG. 8. Apparent viscosity - reciprocal rate of flow curve. Anhydrous sodium stearate in cell A. Ordinate for 236° curve shown $\times 10$.

Plastic flow sets in at temperatures below 298°, the rate not being proportional to the pressure, with the consistency curves concave toward the rate axis; it is non-Newtonian. Neither do the curves extrapolate to the origin, but show a tendency to intercept the pressure axis—that is to say, sodium stearate has a yield value and is behaving as a Bingham body. For non-Newtonians we can calculate, again by the Poiseuille equation, the *apparent* viscosity, at a given temperature and a certain rate of flow, which is the viscosity the sodium stearate would have were it Newtonian.* While apparent viscosity is unreal, it is useful, and the definition has been accepted by many

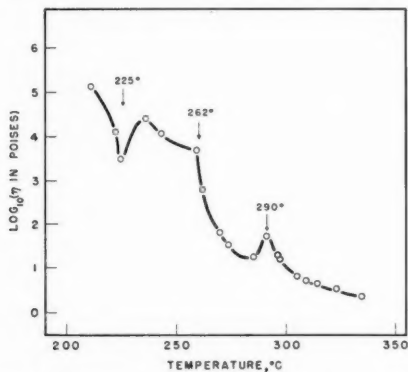


FIG. 9. Residual viscosity - temperature curve. Anhydrous sodium stearate.

*In Fig. 8, curves for 243° and 259° indicate the uselessness of single point determinations of viscosity, which, had they been made here, at the intersection of the curves, would have led to the conclusion that the values were identical at these temperatures. The residual viscosities are quite different.

rheologists. Plotting apparent viscosity against the reciprocal of the rate of flow gives a curve which is linear, initially, with a positive slope (e.g. Fig. 7), eventually approaching a steady value (e.g. Fig. 6), when observations could be made at a sufficiently low rate (high reciprocal rate) of flow. The viscosity at a given temperature falls with increasing rate of flow and the sodium stearate can be considered thixotropic.

While no over-all satisfactory explanation of thixotropy has been given, it is safe to assert that it depends upon structure which has rigidity, and the hypothesis of Goodeve and Whitfield (2), put forward originally for suspensions of carbon black in mineral oil, seems applicable: the rate of structural build-up is proportional to the structural concentration and equals, at equilibrium, the rate of structural breakdown, itself proportional to the rate of flow (S). Further, the structural concentration is assumed to be proportional to the difference between the apparent and residual viscosities; the former (η) has been defined above, and the latter (η_0) is the viscosity at infinite rate of flow when the structure is completely broken up. This theory leads to the equation:

$$\eta = \eta_0 + \theta/S$$

where θ is the coefficient of thixotropy, and also predicts that as $1/S$ increases, the apparent viscosity rises more and more slowly and bends toward a steady value (Fig. 6).

The coefficient of thixotropy is a function of time and structural strength, and is equal to the yield value intercept of the consistency curve. There is some confusion because these authors say that θ is not a yield value, but such a value can be, though not necessarily, due to thixotropy.

Residual viscosity, the viscosity at infinite rate of flow, read from the extrapolated curves of apparent viscosity and reciprocal rate of flow, is seen to vary in a discontinuous manner with temperature* in Fig. 9, covering the range 211° to 336°. There are transitions at 225°, 262°, and 290°, the second corresponding to the transition subneat to neat, for which previously reported values are 255°, 257°, 258°, 260°, and 262° respectively (Table I), and the third, to the melting point—hitherto found at 278° and 288° (Table I). It should be recalled that anhydrous sodium stearate is thixotropic, some 8° above the melting point, at 298°, Newtonian when the temperature has risen to 305°, and the change from plastic to Newtonian flow does not appear to take place at the melting point. Vold (9) assigned the transition that he observed at 226° to the subneat to neat phase change, but since the authors find transitions at 225° and 262°, the generally accepted temperature for this change, it is evident that there is a further transition within the subneat phase at 225°.

It is intended to account theoretically for the phase changes in a subsequent publication.

CONCLUSIONS

1. A viscosity method has been shown to be of use in studying the transition temperatures of anhydrous sodium stearate.

*The plots at 305° and all higher temperatures are for anhydrous sodium stearate as a Newtonian liquid, and the viscosity is, of course, the same at all values of the flow rate.

2. The transition subneat to neat occurs at 262° , and the true melting point at 290° , in agreement with those put forward by earlier workers.
3. A transition within the subneat phase has been found at 225° .
4. Anhydrous sodium stearate exhibits thixotropy over the range 211° to 298° , just above the melting point, and the results agree well with the Goodeve and Whitfield model of this phenomenon.

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PREPARATION OF DINITRO-*n*-ALKYL PHENOLS¹

By G. G. S. DUTTON, T. I. BRIGGS,² B. R. BROWN,³
AND R. K. POWELL⁴

ABSTRACT

The preparation of a series of dinitro-*n*-alkyl phenols is described. The dinitrophenols were characterized as their piperidine, morpholine, and cyclohexylamine salts. In the course of the work some new derivatives of these *n*-alkyl phenols and intermediate hydroxyketones were obtained.

INTRODUCTION

The use of dinitroalkyl phenols as insecticides and herbicides has been widely reported and in order to investigate the variation in their toxicity with chemical structure, a series of dinitro-*n*-alkyl phenols was required in which the alkyl group had from two to eight carbon atoms. Kagy (5) reports the testing of some such compounds but the preparation of such a series has not previously been described.

The preparation of the *n*-alkyl phenols was based on the method of Sandulesco and Girard (8) who subjected the phenyl esters to the Fries rearrangement and reduced the resulting hydroxyketones by the method of Clemmensen. We have found that the intermediate hydroxyketones and resulting phenols were more easily characterized by the derivatives described herein rather than as in the original paper (7). The *n*-alkyl phenols were then nitrated and converted to their amine salts as previously described (3).

One typical synthesis is reported and the relevant data on the cognate preparations are given in Tables I-V.

EXPERIMENTAL*

n-Butyryl Chloride

n-Butyryl chloride was prepared by the method of Helferich and Schaefer as given in Organic Syntheses (4). The commercial acid and thionyl chloride used were each distilled before use.

Phenyl-*n*-butyrate

To pure phenol (1 mole) in a 1 liter flask, fitted with a reflux condenser and a hydrogen chloride trap, was added *n*-butyryl chloride (1.1 mole) over half an hour. The reaction mixture was heated on a steam bath for half an hour and then distilled. After a small forerun of excess acid chloride essentially pure material passed over. The ester was then redistilled, yielding phenyl-*n*-butyrate boiling at 192° C. Yield, 90%.

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*All melting and boiling points are uncorrected.

TABLE I
PHENYL ESTERS

Ester	Yield, %	B.p., °C.	$\eta_D^{25^\circ\text{C}}$
Phenyl acetate	85	192	1.5017
Phenyl propionate	80	206	1.5002
Phenyl- <i>n</i> -butyrate	82	224	1.4934
Phenyl- <i>n</i> -valerate	75	160 (14 mm.)	1.4869
Phenyl- <i>n</i> -caproate	75	260	1.4840
Phenyl- <i>n</i> -heptylate	90	120 (2 mm.)	1.4829
Phenyl- <i>n</i> -caprylate	85	136 (2 mm.)	1.4810

2- and 4-Hydroxy-n-butyrophenone

Aluminum chloride (4 moles) was placed in a two-necked 2-liter flask and heated to 70° C. Phenyl-*n*-butyrate (warmed to 40° C.) was then added as quickly as possible, when the temperature of the mixture rose to 110° C. The reaction mixture was then brought rapidly to 140° C. and kept there for three quarters of an hour. The reaction mixture, which was a glassy mass, was cooled to room temperature and hydrolyzed by the addition of 1500 ml. ice cold 6 *N* hydrochloric acid. Hydrolysis was completed by warming to 70° C. for a quarter of an hour, when a viscous red oil separated. This oil was sepa-

TABLE II
HYDROXYKETONES HO-C₆H₄-COR

Compound	Yield, % ^a	B.p., °C.	M.p., °C.	$\eta_D^{25^\circ\text{C}}$	2,4-Dinitrophenyl-hydrazone		
					M.p., °C.	Nitrogen, % ^{**}	
						Calc.	Found
2-Hydroxyacetophenone	36 ^a	45 (0.1 mm.)	..	1.5570	210
4-Hydroxyacetophenone	50 ^a	160 (1.0 mm.)	107	..	225
2-Hydroxypropiophenone	48 ^a	54 (0.1 mm.)	..	1.5485	189
4-Hydroxypropiophenone	40 ^a	164 (1.0 mm.)	146	..	232
2-Hydroxybutyrophenone	36 ^b	64 (0.1 mm.)	..	1.5379	203
4-Hydroxybutyrophenone	34 ^b	171 (1.0 mm.)	91	..	215
2-Hydroxyvalerophenone	37 ^b	74 (0.1 mm.)	..	1.5310	178	15.65	15.58
4-Hydroxyvalerophenone	41 ^b	160 (1.0 mm.)	62	..	182	15.65	15.59
2-Hydroxycaprophenone	45 ^c	83 (0.1 mm.)	..	1.5262	153†
4-Hydroxycaprophenone	30 ^c	167 (1.0 mm.)	60	..	184
2-Hydroxyheptophenone	51 ^c	94 (0.1 mm.)	..	1.5211	153†	14.50	14.48
4-Hydroxyheptophenone	34 ^c	171 (1.0 mm.)	90	..	174	14.50	14.41
2-Hydroxycaprylophenone	41 ^c	104 (0.1 mm.)	..	1.5170	140	14.00	13.96
4-Hydroxycaprylophenone	34 ^c	183 (1.0 mm.)	59	..	171	14.00	13.99

^aIn carrying out the Fries rearrangement of the phenyl ester, the ester was warmed to (a) 25° C., (b) 40° C., (c) 60° C. before addition to the aluminum chloride which was heated to 70–80° C. in all cases.

^{**}Analyses quoted for new compounds only.

†Mixed melting point gave depression of 9° C.

rated, washed with 6 *N* hydrochloric acid, water, and dried. The dried oil was then fractionated under vacuum using a Bruehl receiver. The 2-hydroxy-*n*-butyrophenone distilled as an oil boiling at 63–65° C. (0.1 mm.) and then 4-hydroxy-*n*-butyrophenone as an oil boiling at 161° C. (1 mm.), which rapidly solidified. The two isomers were then separately redistilled and the 4 isomer on recrystallization gave a melting point of 91° C. Data on the other hydroxyketones are recorded in Table II.

In order to confirm the orientation of the hydroxyketones and hence the phenols derived therefrom by reduction, a sample (1 gm.) of the lower boiling hydroxy-*n*-butyrophenone was dissolved in caustic potash solution and methylated with methyl sulphate. The methyl ether thus formed was oxidized with alkaline permanganate and there was isolated an acid which, on recrystallization from carbon tetrachloride, melted at 101° C., unchanged on admixture with an authentic sample of *o*-methoxybenzoic acid. In a like manner a sample (1 gm.) of the higher boiling, solid hydroxy-*n*-butyrophenone was methylated and oxidized, yielding an acid, m.p. 184–185° C., unchanged on admixture with an authentic sample of anisic acid. Similar oxidations were carried out with each pair of hydroxyketones recorded in Table II.

2- and 4-*n*-Butylphenol

2-Hydroxy-*n*-butyrophenone and the 4 isomer were separately reduced by the Clemmensen method (1, 2) using concentrated hydrochloric acid and amalgamated zinc. In order to reduce the time of refluxing the Martin modification (6) was used whereby some glacial acetic acid was added in order to

TABLE III
n-ALKYL PHENOLS

Phenol	Yield, %	B.p., °C. (1 mm.)	$n_D^{25^\circ\text{C}}$	3,5-Dinitrobenzoate		
				M.p., °C.	Nitrogen, %	
					Calc.	Found
2-Ethyl	72	60	1.5352	107
4-Ethyl	75	76	M.p. 45°C.	139
2- <i>n</i> -Propyl	60	65	1.5280	96	8.48	8.51
4- <i>n</i> -Propyl	72	82	1.5220	123	8.48	8.54
2- <i>n</i> -Butyl	65	75	1.5182	97	8.14	8.16
4- <i>n</i> -Butyl	67	88	1.5160	92	8.14	8.17
2- <i>n</i> -Amyl	88	89	1.5141	98	7.82	7.82
4- <i>n</i> -Amyl	80	97	1.5107	94	7.82	7.84
2- <i>n</i> -Hexyl	84	103	1.5090	95	7.52	7.51
4- <i>n</i> -Hexyl	81	112	1.5055	87	7.52	7.55
2- <i>n</i> -Heptyl	86	115	1.5058	92	7.25	7.26
4- <i>n</i> -Heptyl	75	123	1.5040	97	7.25	7.28
2- <i>n</i> -Octyl	86	126	1.5032	93	7.00	7.01
4- <i>n</i> -Octyl	63	134	M.p. 42°C.	91	7.00	7.05

TABLE IV
 DINITRO-*n*-ALKYL PHENOLS AND THEIR PIPERIDINE SALTS

Phenol	Yield on nitration, %	B.p., °C. (0.1 mm.)	M.p., °C.	Piperidine salt*			
				Formula	M.p., °C.	Nitrogen, %	
						Calc.	Found
4,6-Dinitro-2-ethyl	64	120	36	C ₁₃ H ₁₉ N ₃ O ₅	214	14.14	14.20
2,6-Dinitro-4-ethyl	60	130	36	C ₁₃ H ₁₉ N ₃ O ₅	234	14.14	14.06
4,6-Dinitro-2- <i>n</i> -propyl	71	128	..	C ₁₄ H ₂₁ N ₃ O ₅	186	13.50	13.62
2,6-Dinitro-4- <i>n</i> -propyl	50	141	41	C ₁₄ H ₂₁ N ₃ O ₅	193	13.50	13.56
4,6-Dinitro-2- <i>n</i> -butyl†	67	140	..	C ₁₅ H ₂₃ N ₃ O ₅	148	12.92	12.92
2,6-Dinitro-4- <i>n</i> -butyl	58	152	47	C ₁₅ H ₂₃ N ₃ O ₅	140	12.92	13.03
4,6-Dinitro-2- <i>n</i> -amyl†	60	145	..	C ₁₆ H ₂₅ N ₃ O ₅	138	12.39	12.53
2,6-Dinitro-4- <i>n</i> -amyl	61	166	..	C ₁₆ H ₂₅ N ₃ O ₅	137	12.39	12.50
4,6-Dinitro-2- <i>n</i> -hexyl†	60	162	..	C ₁₇ H ₂₇ N ₃ O ₅	123	11.89	11.96
2,6-Dinitro-4- <i>n</i> -hexyl	49	175	..	C ₁₇ H ₂₇ N ₃ O ₅	154	11.89	11.97
4,6-Dinitro-2- <i>n</i> -heptyl	60	171	..	C ₁₈ H ₂₉ N ₃ O ₅	121	11.44	11.39
2,6-Dinitro-4- <i>n</i> -heptyl	52	184	..	C ₁₈ H ₂₉ N ₃ O ₅	157	11.44	11.56
4,6-Dinitro-2- <i>n</i> -octyl†	51	178	..	C ₁₉ H ₃₁ N ₃ O ₅	125	11.02	11.10
2,6-Dinitro-4- <i>n</i> -octyl	45	192	..	C ₁₉ H ₃₁ N ₃ O ₅	141	11.02	11.04

*All the salts are red, orange, or yellow.

†Ref. (7).

 TABLE V
 MORPHOLINE AND CYCLOHEXYLAMINE SALTS OF DINITRO-*n*-ALKYL PHENOLS*

Dinitrophenol	Morpholine salt				Cyclohexylamine salt			
	M.p., °C.	Formula	Nitrogen, %		M.p., °C.	Formula	Nitrogen, %	
			Calc.	Found			Calc.	Found
4,6-Dinitro-2-ethyl	191	C ₁₂ H ₁₇ N ₃ O ₆	14.05	14.02	176	C ₁₄ H ₂₁ N ₃ O ₅	13.50	13.49
2,6-Dinitro-4-ethyl	217	C ₁₂ H ₁₇ N ₃ O ₆	14.05	14.05	190	C ₁₄ H ₂₁ N ₃ O ₅	13.50	13.57
4,6-Dinitro-2- <i>n</i> -propyl	167	C ₁₃ H ₁₉ N ₃ O ₆	13.42	13.56	185	C ₁₅ H ₂₃ N ₃ O ₅	12.92	12.96
2,6-Dinitro-4- <i>n</i> -propyl	165	C ₁₃ H ₁₉ N ₃ O ₆	13.42	13.40	178	C ₁₅ H ₂₃ N ₃ O ₅	12.92	12.90
4,6-Dinitro-2- <i>n</i> -butyl	169	C ₁₄ H ₂₁ N ₃ O ₆	12.84	12.82	175	C ₁₆ H ₂₅ N ₃ O ₅	12.38	12.45
2,6-Dinitro-4- <i>n</i> -butyl	134	C ₁₄ H ₂₁ N ₃ O ₆	12.84	12.84	148	C ₁₆ H ₂₅ N ₃ O ₅	12.38	12.44
4,6-Dinitro-2- <i>n</i> -amyl	158	C ₁₅ H ₂₃ N ₃ O ₆	12.32	12.47	164	C ₁₇ H ₂₇ N ₃ O ₅	11.90	11.84
2,6-Dinitro-4- <i>n</i> -amyl	132	C ₁₅ H ₂₃ N ₃ O ₆	12.32	12.32	154	C ₁₇ H ₂₇ N ₃ O ₅	11.90	11.91
4,6-Dinitro-2- <i>n</i> -hexyl	155	C ₁₆ H ₂₅ N ₃ O ₆	11.83	11.90	176	C ₁₈ H ₂₉ N ₃ O ₅	11.44	11.35
2,6-Dinitro-4- <i>n</i> -hexyl	150	C ₁₆ H ₂₅ N ₃ O ₆	11.83	11.93	135	C ₁₈ H ₂₉ N ₃ O ₅	11.44	11.49
4,6-Dinitro-2- <i>n</i> -heptyl	146	C ₁₇ H ₂₇ N ₃ O ₆	11.38	11.46	175	C ₁₉ H ₃₁ N ₃ O ₅	11.02	11.08
2,6-Dinitro-4- <i>n</i> -heptyl	148	C ₁₇ H ₂₇ N ₃ O ₆	11.38	11.49	125	C ₁₉ H ₃₁ N ₃ O ₅	11.02	11.04
4,6-Dinitro-2- <i>n</i> -octyl	148	C ₁₈ H ₂₉ N ₃ O ₆	10.97	11.02	158	C ₂₀ H ₃₃ N ₃ O ₅	10.63	10.60
2,6-Dinitro-4- <i>n</i> -octyl	135	C ₁₈ H ₂₉ N ₃ O ₆	10.97	11.04	120	C ₂₀ H ₃₃ N ₃ O ₅	10.63	10.65

*All the salts are red, orange, or yellow.

increase the solubility of the hydroxyketone. The yield of 2-*n*-butylphenol was 65% and of the 4 isomer 67%. Details of these and the other phenols are given in Table III.

Dinitro-n-alkyl Phenols

The *n*-alkyl phenols were nitrated in glacial acetic acid as described in a previous communication (3). Most of the nitro compounds were liquids and these were characterized by conversion to piperidine, morpholine, and cyclohexylamine salts (3). See Tables IV and V for details.

ACKNOWLEDGMENTS

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AN APPARATUS FOR THE MICROANALYSIS OF GAS MIXTURES¹

BY M. J. MARSHALL² AND G. CONSTABARIS³

ABSTRACT

An apparatus for the microanalysis of gas mixtures is described with which volumes of gases as low as 5 cu. mm. at N.T.P. can be analyzed in the dry way. Two applications of the method are presented; the first is for carbon dioxide, the second is for the use of the diffusion of hydrogen through palladium in the presence of either carbon monoxide or methane for the analysis of hydrogen.

INTRODUCTION

Marshall and Findlay (5) have briefly described an apparatus for the microanalysis of gas mixtures by dry methods. The purpose of this paper is to describe in more detail this apparatus in an improved form, and to present its application for the analysis of carbon dioxide, and of hydrogen in the presence of carbon monoxide or methane.

The apparatus described here was designed to be used in the volume range of 5 to 40 cu. mm. It will be evident from the description to be given that this range can be moved in either direction by altering the dimensions of the gauge. The method of analysis lends itself most readily to the study of gases occurring in high-vacuum systems, but its use could be made quite general with the development of suitable methods for introducing small gas samples into the apparatus.

APPARATUS AND METHOD

The apparatus is shown in Fig. 1. It consists of a McLeod gauge which has as its small volume the leg *A* of a three-way capillary stopcock *S*. The leg *C* leads to high vacuum or air through the aligned ground-glass joints *J*. (This type of connection permits the easy removal and reassembly of the gauge whenever cleaning is necessary.) The leg *B* is pulled down in a straight taper as close to the barrel of the stopcock as possible. This taper forms the inner part of a ground-glass connection, the outer part of which is the main line to which the analysis tips are connected, by means of the small ground-glass joints *D, E, F, G, H*. The analysis assembly is shown in Fig. 2. The ground-glass joints were hand made. They are identical in size to the tapered part of an ordinary lead pencil. The accessory pumps and lines are not shown.

The inner part of joint *D* is soft glass, into which is sealed a small palladium tube closed at the upper end. The tube is about 5 cm. in length, 1 mm. I.D., 2 mm. O.D. The tube is heated by a small heater made from a few turns of nichrome wire on a quartz sheath which fits fairly loosely over the palladium tube. The temperature is measured with a thermocouple inserted into the heater so that its junction is close to the tube. The inner part of joint *E* is connected very close to the microstopcock which in turn is connected through

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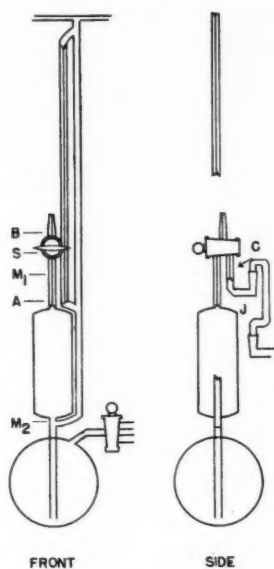


FIG. 1. Modified McLeod gauge as a micro gas analysis apparatus.

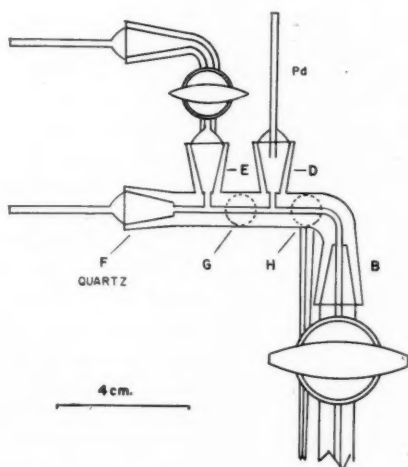


FIG. 2. Detail of analysis assembly.

a ground-glass joint to an analysis tip containing an intimate mixture of silver oxide and hopcalite. The inner part of *F* is made from quartz tubing. This analysis tip holds a small piece of copper wire with its surface oxidized. The tip is heated with a small air-gas flame. The inner part of joint *G* is connected

to a pyrex tip containing a dry solid solution of lithium, sodium, and potassium hydroxides. This tip is heated with a heater similar to the one described for the palladium tube. The inner part of *H* is drawn down to a very fine capillary about 8 in. long. This tip is bent into a vertical position and is used as a liquid air trap. The ground-glass joints are sealed with picene and the precision made stopcock *S* is lubricated with Apiezon "L". (Apiezon wax "W" would be an excellent substitute for the picene. The Apiezon lubricants are available from James G. Biddle and Co., Philadelphia, Pa.; the picene is distributed by Schrader and Ehlers, 239 Fourth Avenue, New York City.) The total volume above the stopcock is 1.39 cc.

The McLeod gauge was calibrated in the accepted manner. The total volume of the gauge is 216.6 cc. and the volume from the plug of the stopcock to the zero mark on leg *A* of *S* is 0.0983 cc. This mark is shown as M_1 on Fig. 1. A pressure of 1 cm. of mercury read at M_1 at 20° C. represents 1.205 cu. mm. at N.T.P. The upper limit of gas volume when read at M_1 is 40 cu. mm. but this can be greatly extended by the use of a zero mark further down leg *A*.

The general method of operating the apparatus is as follows. A gas sample is introduced into the highly evacuated apparatus, and its pressure read by raising the mercury to M_1 with *S* closed. The mercury is then lowered a safe distance and *S* is opened. The mercury is periodically raised and lowered a bit to move the gas about the analysis train while the analysis process is taking place. The mercury is never allowed to run through the plug of *S*. When the analysis process is completed the mercury is lowered carefully to the gauge cutoff M_2 , and is left in this position for a few minutes. *S* is closed and the new pressure is read at M_1 . The change in pressure reading represents the fraction of the constituent being analyzed.

This method of operation involves an error arising from the volume of the analysis assembly, since part of the residual gas remains in the analysis tips. For this apparatus the error is approximately 0.5%. This is the reason that the volume of the analysis assembly must be kept as small as possible. However, there is no error caused by this volume if, when the sample is first admitted to the gauge, the mercury is held at M_2 , *S* is opened for a short time, then closed, and the initial pressure read at M_1 . This procedure, which changes the pressure volume relation given above slightly, can be used if none of the constituents react in the analysis assembly at room temperature. Alternatively, if a constituent does react at room temperature the error can be lessened by separating the particular analysis tip by a microstopcock.

In any case, two other circumstances lead to the necessity of a small analysis assembly volume. First, the lower limit of gas volume that can be analyzed rises with the volume of the tips. Second, it is desirable to carry out the analysis processes at as high a pressure as possible. It is evident that the pressure during analysis varies inversely as the volume of the analysis assembly.

It is seen that the analysis reactions must be carried out in the dry way; water vapor cannot be tolerated in the system.

The older forms of this apparatus used neither ground-glass connections nor the stopcock *S* (5). The use of the stopcock greatly reduces the quantity of gas that can be analyzed. The use of the small ground-glass joints is not only

convenient for the removal of the analysis tips but is also necessary in any analysis process requiring the heating of the tip. When the picene is heated it decomposes, admitting gases to the system at a rate proportional to the area exposed to the vacuum. In a ground-glass joint this area is negligible; in this apparatus the picene has given no trouble. This was not the case before ground-glass connections were used.

THE ANALYSIS OF CARBON DIOXIDE

In this apparatus the best method for the analysis of carbon dioxide is by condensation at liquid air temperature in the analysis tip connected at *H*. After the initial pressure is read and *S* is opened, the liquid air is placed so that its level is about 2 in. above the bottom of the tip. After a few minutes the liquid air level is raised an inch or so and this procedure is continued until the complete vertical portion of the tube is submerged. If the whole tip is submerged immediately, the carbon dioxide will solidify at the liquid air level and will clog the capillary. This does not permit the uncondensed portion of the gas to reach an area of sufficiently low temperature to solidify. The method is accurate and quick but its main disadvantage is that it is not selective.

A selective reagent for carbon dioxide is alkali metal hydroxide. However, the dry hydroxide must be melted before it will absorb carbon dioxide, and at the high melting points of these hydroxides their rate of attack on the glass analysis tip is great. The advantage of hydroxide absorption over liquid air condensation was great enough to warrant a search for a mixture of hydroxides that would melt at a low temperature. A very brief investigation by means of cooling curves of ternary systems of almost dry hydroxides showed that a mixture could be obtained with a melting point under 100° C., at which temperature the rate of glass attack was not marked. The method of preparing the reagent was to fuse together 2.6% lithium hydroxide, 23.6% sodium hydroxide, and 73.8% potassium hydroxide. The melt was allowed to cool to 75° C. and was held at this temperature for an hour. The supernatant liquor was decanted from the solid phase that had settled out. On cooling a few degrees the liquor solidified. The solid was the absorption reagent used. When first put in the analysis tip it must be outgassed in a molten condition to remove the water it absorbs while being handled. Carbon dioxide was prepared by subliming commercial dry ice into a thoroughly outgassed storage bulb.

Preliminary tests led to the following observations. The slight amount of water vapor given off on melting readily reabsorbed in the reagent when it solidified. Therefore, the correct procedure in an analysis was not to lower the mercury from M_1 to M_2 until the reagent had solidified. Also, the reagent absorbed carbon dioxide extremely slowly at room temperature. The absorption rate did not become significant until a temperature of 65° C. was reached. This showed that there was no necessity of separating the reagent from the main analysis line by means of a microstopcock. At 70° C. 20 cu. mm. of carbon dioxide at S.T.P. would absorb in five minutes.

A comparison of the analysis of carbon dioxide in mixtures with air, by liquid air condensation and hydroxide absorption, is given in Table I. The absorption temperature was 70° C.–100° C. The time at temperature was

TABLE I
COMPARISON OF ANALYSIS OF CARBON DIOXIDE BY
HYDROXIDE ABSORPTION AND BY CONDENSATION

Sample volume, cu. mm. at N.T.P.	% CO ₂ by absorption	% CO ₂ by condensation
18.9	61.9	62.5
18.2	35.7	35.7
17.8	67.2	68.0
16.3	78.5	78.5
13.5	51.2	51.2
13.3	39.1	39.1
10.3	57.5	57.5
3.2	83.5	82.0

five minutes and the mercury was not lowered until five minutes after the heater was turned off.

It is apparent that the reagent is satisfactory with regard to analysis, attack on glass, and time for analysis.

ANALYSIS OF HYDROGEN BY DIFFUSION THROUGH PALLADIUM

Smithells (6) states that the rate of diffusion of hydrogen through palladium becomes appreciable only at temperatures above 260° C. and that at 500° C. the palladium slowly loses its permeability. The use of palladium for the analysis of hydrogen in the presence of carbon monoxide, methane, and stopcock grease apparently presents some difficulties. Stopcock greases and hydrocarbons have been shown to poison the diffusion process (1). Fleiger (3) constructed an analysis apparatus with which the analysis of hydrogen by diffusion through palladium was attempted. It was found that an accurate determination of hydrogen in the presence of carbon monoxide and methane could be obtained only if not over 5% of methane or 9% of carbon monoxide were in the gas mixture. These limitations were attributed to the following reactions catalyzed by palladium at 300° C.: (1) $2\text{CO} = \text{CO}_2 + \text{C}$; (2) $\text{CO} + 3\text{H}_2 = \text{H}_2\text{O} + \text{CH}_4$; (3) $\text{CH}_4 = \text{C} + 2\text{H}_2$. However, Taylor and McKinney show that reactions (1) and (3) do not occur on massive palladium at 300° C. (7).

The apparatus described here uses quite low pressures of reactants, and the greases used have very low vapor pressures. For these reasons, it was believed the above considerations would not apply under the analysis conditions of this apparatus and the analysis of hydrogen could be effected in the presence of methane and carbon monoxide.

Hydrogen was obtained by the reaction of water on potassium. A small piece of clean potassium was sealed into a side tube connected by a narrow arm to a small reaction vessel in the vacuum system. The potassium was distilled, with the pumps on, into the reaction tube. The side tube was removed by collapsing the narrow arm, and pure water vapor was admitted to the reaction vessel. The hydrogen was expanded into an outgassed storage bulb through a liquid air trap. Its purity by copper oxide oxidation, and by diffusion through palladium, was 99.9%.

Methane was prepared from methyl magnesium iodide. The Grignard reagent, in an ether solution, was placed in a side tube connected to the vacuum system. The solution was frozen with liquid air and the side tube was sealed. The system was well evacuated and the liquid air removed and placed on another side tube into which the ether then distilled. The residue in the first tube was a colorless amorphous solid. The frozen ether was removed by collapsing the side arm and water vapor was admitted to the solid methyl magnesium iodide. The resulting methane was expanded into an evacuated storage bulb through a liquid air trap. The purity of the methane was 99.6% by copper oxide oxidation and condensation of the carbon dioxide by liquid air.

Carbon monoxide was prepared by the method of Thompson (8). Formic acid vapor was passed through outgassed phosphorus pentoxide. The carbon monoxide produced was passed through a liquid air trap into an outgassed storage bulb. Inexplicably the carbon monoxide so produced contained about 2% by volume of hydrogen. This impurity was shown to be hydrogen by a shrinkage in volume on copper oxide oxidation, the products of which condensed completely at liquid air temperature, and by the same shrinkage when subjected to the heated palladium tube. The last effect could not be due to reaction (1) above because no carbon dioxide was produced, nor could the shrinkage be increased by prolonged reaction times. After the hydrogen had been removed by diffusion through palladium the carbon monoxide was 99.9% pure. The data given below show conclusively that reaction (2) did not occur during this process.

The initial experiments with pure hydrogen showed that at an initial pressure of hydrogen of 1.5 cm. of mercury 15 min. was sufficient to remove completely 20 cu. mm. of hydrogen.

TABLE II
ANALYSIS OF HYDROGEN IN THE PRESENCE OF METHANE OR CARBON MONOXIDE

% by volume			Sample vol., cu. mm. at N.T.P.	Time, min.	Temperature, °C.	% H ₂ found
H ₂	CO	CH ₄				
41.7		58.3	21	10	410	42.2
69.8		30.2	20.6	10	370	71.7
2.4		97.6	6.5	5	360	3.9
70.0		30.0	22.0	6	340	70.0
35.3		64.7	20.8	15	310	35.3
80.8		19.2	31.5	15	310	80.8
85.7	14.3		8.6	7	380	85.7
82.9	17.1		9.6	20	310	82.9
78.1	21.9		4.2	5	380	78.1
67.0	33.0		5.0	6	385	67.0
59.8	41.2		5.5	3	390	59.8
52.0	48.0		6.5	6	390	52.0
50.0	50.0		7.8	3	370	50.0
44.3	55.7		12.2	11	310	44.3
43.6	56.4		8.0	6	360	43.6
34.3	65.7		10.8	3	380	35.1
33.3	66.7		9.9	3	430	31.5

Standard mixtures of hydrogen and methane, and of hydrogen and carbon monoxide were made and analyzed for hydrogen under varying conditions of concentration and temperature. The results are given in Table II. The time noted is that taken to give constant readings for the final pressure on the McLeod gauge.

It is evident that hydrogen can be accurately analyzed in this apparatus in the presence of carbon monoxide over the entire concentration range. If hydrogen is analyzed in the presence of methane by this method accurate determinations can be made over the concentration range by not using the palladium tube at a temperature higher than 325° C. Higher temperatures lead to high hydrogen results because of the decomposition of the methane.

The following points of interest concerning this apparatus are stated without presenting data. The use of copper oxide as an oxidant in gas analysis is well known and its use is successful in this particular apparatus. The oxidation of carbon monoxide at room temperature by a silver oxide - hopcalite mixture has been used with good results in the older form of the apparatus (2). More recently red mercuric oxide has been proposed for this purpose (4).

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ON THE MECHANISM OF THE DISSOLUTION OF MAGNESIUM IN ACIDIC SALT SOLUTIONS

I. PHYSICAL CONTROL BY SURFACE FILMS¹

BY E. J. CASEY AND R. E. BERGERON

ABSTRACT

A kinetic study and analysis has been made of the effects of ionic strength, acid activity, temperature, and salt type on the dissolution of magnesium in acidic salt solutions. This is an example of the simplest type of corrosion involving hydrogen evolution. The results are interpreted in terms of the effects of the various factors on the structure of a surface film which must be magnesium oxide and/or hydroxide even in acidic solutions. The importance of internal dissolutions in the film at high concentrations of attacking reagent, for this and other cases, is shown. Owing to complex formation, under certain conditions an odd case of "chemical control" of the dissolution rate in this simplest case becomes evident. Corrosion potential measurements aid in the interpretation.

INTRODUCTION

According to King and co-workers (12), who support a modification of the diffusion-layer theory originally due to Noyes and Whitney (18), and Nernst (17), the experimental support for probable diffusion control of the rate of dissolution of metals in acidic aqueous solutions rests on the following facts. For convenience these are reproduced in part from the recent paper by Roald and Beck (19).

1. Different solids dissolve at nearly the same rate in the same reagent under the same conditions.

2. Increased stirring increases the rate. That the rate of dissolution in many cases is a linear function of linear velocity, except at very low linear velocity, has been demonstrated for some cases by the data of King *et al.* (12), Garrett and Cooper (5), Roald and Beck (19), and others. The rate is usually expressed as the constant of the first order rate expression

$$dn/dt = k.A.c,$$

where c is the acid concentration, A the area of the specimen, dn/dt the dissolution rate.

3. The rate of dissolution has been found for many cases to be nearly inversely proportional to the viscosity of the solution for a number of solutions.

4. The rates of dissolution in acid solutions seem to follow the diffusion coefficients of the acid through the solution, perhaps even more closely than they follow the acid strength.

5. Temperature coefficients have been found by many investigators to be of the order usually associated with a controlling step which is some physical transport process. Temperature coefficients are usually of the order of 3000 to 5000 cal./mole.

It should be noted that these criteria do not eliminate all but diffusion control. These criteria could apply equally well to any type of mass transfer

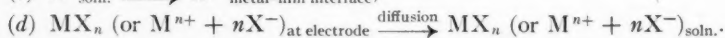
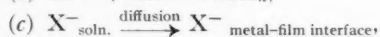
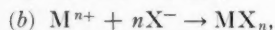
¹ Manuscript received April 17, 1953.

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step which is part of the dissolution process. That the rates follow roughly the diffusion coefficients of the acid through the solution indicates that the control of the process is related in some manner to the physical structure of the solutions. However, the rate of dissolution might well be controlled by any physical step whose rate, in turn, is dependent upon the changing structure of the surface film. Each of the criteria listed above refers indirectly to the effects produced by changes in the properties of this surface layer. For instance, King and Cathcart (11) measured (a) the diffusion coefficient of the acid, and (b) the rates of dissolution of magnesium in a series of solutions. The diffusion coefficients of the acids in the bulk solution were found to increase as the rates of dissolution increase. This was interpreted by the authors as indicating that the rate is controlled by diffusion of hydrochloric acid through the solution, but might perhaps better be interpreted more broadly as being evidence that the molecular structure of the surface film is being reflected by the structure of the bulk solution: the diffusion coefficient of any particle through the film, if it could be measured, would reflect the rate of the dissolution process, since changes in the rate of passage of any particle through the film reflect changes in the structure of the film. Hence, in the over-all process of dissolution, any one of the successive steps whose rate is affected by changes in the physical and electrical properties of the film, by the above criteria, may be in fact the rate-determining step.

A consideration of the first order rate constants listed in various papers indicates that in some cases the values taken at different intervals of time are subject to drift, and that in other cases the values listed are for less than 20% of complete reaction. In either case this would indicate that, although the calculated first order rate constants give a fairly accurate method of measuring temperature coefficients, for example, the evidence for first order dependence (in time) of rate on acid concentration is not good, and, in some cases, poor. Also in previous work there does not seem to be any attempt to isolate the effect of acid strength from the ionic strength of the solution. Hence, a further study of the dissolution of a base metal in acidic solutions with these factors in mind seemed to be indicated.

Consider the simplest case involving hydrogen evolution where only one anodic process and one cathodic process occur.* The anodic process may be pictured as being the sum of the following steps:



The corresponding cathodic process may be pictured as being the sum of the following steps:

*That dissolution of such metals is electrochemical in nature, that is that local anodes and cathodes exist on the metal surface during dissolution, is now well established since the work of Thiel and Eckell, Müller, and others (15).

- (a) H^+ solvated, in soln. $\xrightarrow{\text{diffusion}}$ H^+ solvated, metal-soln. interface,
 (b) H^+ solvated, metal-soln. interface $\xrightarrow{\text{adsorption}}$ H^+ adsorbed,
 (c) $H^+_{\text{ads.}} + e \rightarrow H_{\text{ads.}}$,
 (d) $2H_{\text{ads.}} \xrightarrow{\text{recombination}} H_{2\text{ ads.}}$,
 (e) $nH_{2\text{ ads.}} \xrightarrow{\text{desorption}} nH_2\text{ dissolved}$,
 (f) $H_2\text{ dissolved} \xrightarrow{\text{hydrogen removal}} H_2\text{ into the atmosphere}$.

When the over-all process is physically controlled, a consideration of the local anodic steps indicates that either (c) or (d) could be the step which controls the over-all rate. In the case of local cathodes the only steps which are probably not physical in nature are (b), (c), and (d), the exact mechanisms of which comprise also the familiar and difficult problem of hydrogen over-voltage. Where physical control is indicated, any of the remaining cathodic steps might control the over-all rate. In such cases, because of the interdependence of the various steps, the film-type of polarizations which determine the rate must in turn be determined by the rates of the various steps which produce and destroy the film. Since the rate of each step is so critically dependent upon the rates of the rest, and since this type of steady state must involve many transport steps proceeding at nearly the same rate, a change in conditions which affects the slowest step could easily result in a readjustment in which some other step becomes rate-determining in a new steady-state condition. Both minor and major readjustments of the structure of the rate-controlling film are to be expected with changing conditions. Hence the physical properties of the surface film, and the polarizations of local anodes and cathodes, may vary quite markedly with changing experimental conditions of temperature, pressure, electrolyte, electrolyte concentration, metal impurities, etc.

Analogous cases or conditions in which the indications are that the controlling step is not some physical process are uncommon. Thus, Abramson and King (1) found that under conditions of very high linear velocity of the dissolving metal, where the rate of stirring was phenomenally high, iron dissolves in acidic salt solutions at rates which are "chemically" controlled, if activation energies of the order of 12 kcal./mole be the criterion; at low linear velocities the activation energies for the iron dissolution are those of a physically controlled process, with temperature coefficient ~ 5000 cal./mole. In their studies of depolarizers Hochberg and King (8) found cases where both chemical control and physical control seemed to be indicated by the velocity of the reactions.

In cases in which the rate of the dissolution is physically controlled by the film, under any conditions of dissolution the film must be composed of anodic reaction products, MX_n , and/or gas nuclei and bubbles. Hence a knowledge of the factors which influence the structure of the surface film would help in an attempt to elucidate the mechanism of this "simplest case" of corrosion involving hydrogen evolution. The work of Whitby (23), which showed that in acid solutions magnesium corrodes without oxygen consumption, and the

present work, which includes corrosion rates measured by both weight loss and hydrogen evolution techniques, have indicated that the dissolution of magnesium in acidic salt solutions, at least under the conditions chosen for this work, is an example of the simplest case, involving only one anodic process (liberation of magnesium) and only one cathodic process (hydrogen gas evolution).

EXPERIMENTAL METHODS

The magnesium used was the commercially pure, distilled metal obtained from Dominion Magnesium, Ltd., Haley, Ontario. Specimens were prepared by first filing, then mechanically polishing with 00 emery paper, and then etching in 0.5 *N* hydrochloric acid until the surface was bright and clear and the polycrystalline structure of the magnesium clearly visible. Surfaces prepared in this manner gave quite reproducible results on the same metal piece, but pieces with different crystalline faces visible showed the expected small differences in rates of dissolution. These differences have been eliminated experimentally in the data recorded. A surface coating (#323 Stop-Off Lacquer, made by United Chromium, Inc.) was used to protect those portions of the magnesium samples which were not to undergo corrosion.

Solutions were prepared from reagent grade salts and were made up to the desired acid concentration by adding small quantities of the respective acid. Thus nitric acid was used to adjust the pH of the potassium nitrate solutions, and hydrochloric acid for the potassium chloride and magnesium chloride solutions. Thus the pH could be adjusted without the addition of any foreign anion to the solution. Measurements were made with the use of a Beckman Glass Electrode pH Meter, Model H2.

Different types of magnesium samples were used in the dissolution experiments in which weight losses were recorded.

1. A magnesium cylinder was spun at a linear velocity of 40 cm. sec.⁻¹ in an overflowing solution, which was continuously being replenished with fresh solution fast enough to maintain a constant pH. For this work the magnesium sample was 0.38 cm. in radius, and 1.20 cm. in length; the neck was smaller in diameter. The bottom of the cylinder and the neck were protected by the surface coating.

2. Round, flat magnesium pieces were placed in 40 ml. portions of unstirred solutions and the horizontal face allowed to dissolve for certain time intervals. The pH of the solutions was recorded before and after each experiment. The round, flat samples were approximately 1.5 cm. in diameter and 0.6 cm. thick. The sides and bottoms of these pieces were lacquered.

3. Similar experiments to those described in 2 were carried out using square, flat magnesium pieces. The dimensions of these pieces were 1.7 cm. \times 1.7 cm. \times 0.60 cm., with sides and bottom lacquered so that corrosion could take place only from the upper horizontal face.

4. For the combined rate-corrosion potential measurements, oblong magnesium sticks were used. These were 3.5 cm. long and 0.4 cm. square in cross section, and were partially immersed vertically in 40 ml. of the stagnant solutions.

To check the weight loss method, a gas evolution technique was employed. In these experiments, square, flat magnesium pieces corroded in 40 ml. stagnant solutions of magnesium chloride and in each case the volume of water displaced by the evolved gas was recorded as a function of time. Again in these experiments, only one horizontal face was exposed to the solution.

The corrosion potentials of magnesium pieces were measured against silver-silver chloride probe electrodes containing 1 *N* potassium chloride. The probe electrodes were used to prevent any contamination of the magnesium by dissolved silver chloride. The potentials measured were reduced approximately to the hydrogen scale, an activity correction having been made by the Nernst equation; the liquid junction potential, probably of the order of a few hundredths of a volt, was ignored.

A conductivity bridge made by Industrial Instruments Inc., Jersey City, N.J., Model RC-8, was used for conductivity measurements. For salt concentrations below 0.1 molal, a conductivity cell with a constant of 0.0538 was used, while for concentrations above 0.1 molal a cell with a constant of 49.7 was used.

In the overflow system employed for the spinning cylinder, the rates are true initial rates since fresh solution was continually being supplied to the corrosion chamber. In the cases of stationary metal pieces and unstirred solutions, it was found that, in the short times needed for the measurement of the initial rate in potassium chloride, potassium nitrate, and dilute magnesium chloride solutions, the pH of the solutions did not change by more than one or two tenths of a pH unit, and hence the rate through zero time truly referred to the rate of the original pH. The odd effects found in high concentrations of magnesium chloride are considered in the discussion section.

EXPERIMENTAL RESULTS AND DISCUSSION

Potassium Chloride Solutions

Using the constant flow and spun cylinder technique the dependence of rate upon concentration of potassium chloride, at constant acid strength, was obtained. At pH = 3.5 and at linear velocity of 40 cm./sec. the weight losses were of the convenient order of a few milligrams, and the rates obtained as a function of concentration are shown in Fig. 1. That the maximum in the curve is not a function of the physical structure* of the solution was indicated by the fact that the conductivity measurements on the same solutions (Fig. 1) showed no such concentration dependence. That the inhibition of the corrosion at higher concentrations must be simply a modification of the physical step which controls the over-all dissolution was shown by the temperature dependence of the dissolution rate, Table I. The general shape of this type of rate vs. concentration curve is well known from the work of Abramson and King (1), and the present data are plotted in this same sense in Fig. 2. The information from Fig. 3 shows that the smallest activation energies exist at the concentration corresponding to maximum rate at each temperature.

*For discussions on the extent and nature of associations and cross-linkages in water and its solutions, and their effects on rates of transport processes, the reader is referred to the original work of Bernal and Fowler (3), to the recent papers of Weyl (22), and to the modern interpretations of Glasstone, Laidler, and Eyring (6).

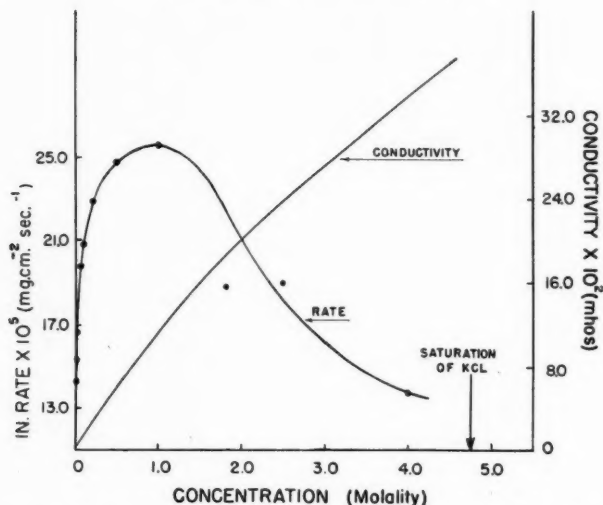


Fig. 1. Initial rate of dissolution and conductivity of solution as a function of salt concentration for magnesium cylinder spun at linear velocity of 40 cm./sec.; constant flow technique, pH = 3.5. Temperature 25°C.

TABLE I

Molality KCl	Initial rate of dissolution $\times 10^{+3}$ (mgm. cm. ⁻² sec. ⁻¹)*, pH = 2.0			
	0°C.	25°C.	40°C.	55°C.
0	1.50	2.30	3.03	3.91
1.0	1.85	2.78	3.53	4.38
3.0	0.92	1.48	1.87	2.25

*The rates recorded are average values of three to five experimental determinations.

That the depression of rate of dissolution at high concentrations is not some mechanical effect due to the spinning cylinder was shown by the fact that this same trend occurs in unstirred solutions when the metal piece was held stationary. Since the rates are considerably lower than in the spun-cylinder experiments at pH = 3.5, acid strength of pH = 2.0 and horizontal flat pieces of magnesium were used consistently. Typical data for initial rates as a function of concentration in unstirred solution at pH = 2.0 are shown in Fig. 4. That the depression of rate at high concentration of salt is not a unique function of chloride ion concentration was shown by the fact that the same trend occurs also in potassium nitrate solution. At this temperature, 25°C., the complexing agent versene was found, oddly enough, simply to depress the dissolution rate at all concentrations, although there is slight indication that in 3 molal solution versene had less of a depressing effect. The nonionic surface-active agent triton NE simply increased the rate in all concentrations, perhaps the lower concentrations more than the higher.

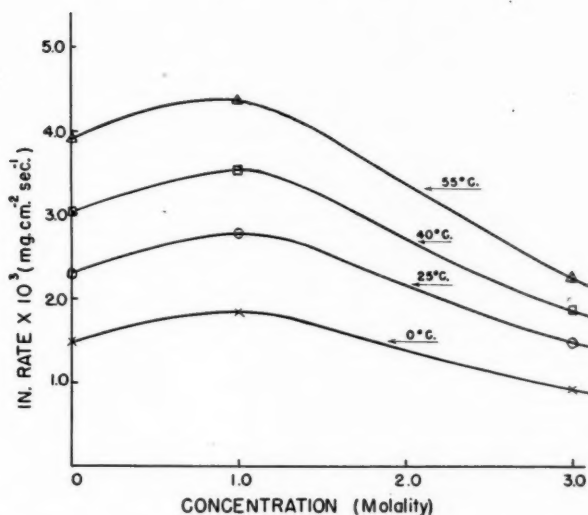


FIG. 2. Initial rate of dissolution as a function of salt concentration for spinning magnesium cylinder in solutions at various temperatures. Constant flow technique, pH = 2.0.

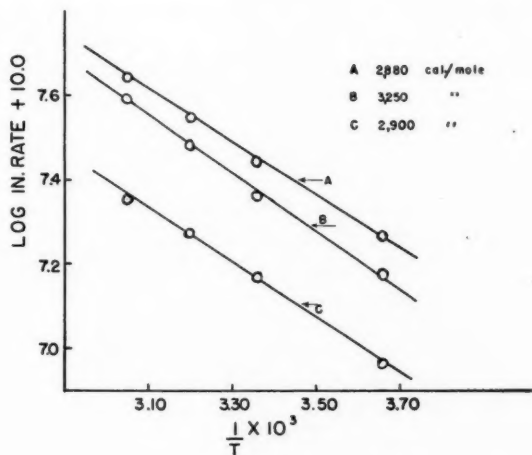


FIG. 3. Arrhenius plots of initial rates of dissolution in potassium chloride solutions; spinning cylinder, constant flow technique, pH = 2.0. A: 1.0 molal potassium chloride; B: 0.0 molal potassium chloride; C: 3.0 molal potassium chloride.

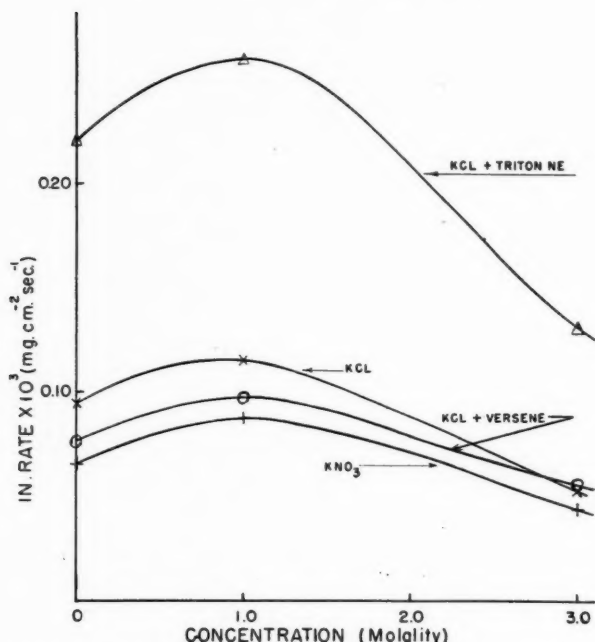


FIG. 4. Initial rate of corrosion of flat, horizontal faces of magnesium as a function of concentration for unstirred potassium chloride and potassium nitrate solutions. Temperature 25°C.

The existence of a maximum in the rate-concentration curve for magnesium in potassium chloride solutions was apparently first noted by Hughes (10) who ascribed the phenomenon to "the catalytic effect of the salt". Since then a similar maximum has been noted in other cases, of which perhaps the most complete figures are reported by Abramson and King (1) on the dissolution of iron in acidic solutions. The apparent dependence of rate of dissolution of magnesium upon the solubility of magnesium hydroxide was suggested by Whitby (24) from work on potassium hydroxide, potassium sulphate, potassium chloride, and other salt solutions. Huber (9) has recently shown by X-ray diffraction and electron diffraction studies that the anodic process of magnesium, in alkaline solutions at least, proceeds by the series of steps $\text{Mg} \rightarrow \text{MgO} \rightarrow \text{Mg}(\text{OH})_2$, that the production of MgO is the primary step.

The facts noted above—the increase, the maximum, and the decrease in rate of dissolution with increasing salt concentration (or increasing ionic strength)—are quite consistent with the assumption that during dissolution the rate is controlled by a surface film of magnesium oxide and/or hydroxide, for it is known (14) that (a) the solubility of magnesium hydroxide in water increases with increasing concentration of various salts, and yet (b) magnesium hydroxide is much less soluble in the presence of saturated solutions of salts

such as sodium chloride and potassium nitrate. Thus a maximum exists in the curve of solubility of magnesium hydroxide vs. salt concentration in solutions of many salts. That the controlling film must be liquidlike, perhaps gelatinous in nature is seen from the fact that the activation energies are all of the order of 3000 cal./mole. Thus, if one assumes that the rate of solution of the film is proportional to its solubility, the facts shown in Figs. 1, 2, and 4 can be qualitatively explained in terms of a diffusion layer which is essentially magnesium oxide and/or magnesium hydroxide, even in a bulk solution which is acidic at pH = 2. The work of other investigations has indicated similar effects. For example Müller (16) has discussed corrosion data on iron and aluminum in terms of porous films of oxide and/or hydroxide in acid concentrations even as high as 4 *N* hydrochloric acid.

Further insight into the nature of the rate-determining step and the nature of the film was obtained from a study of the dependence of the rate of dissolution upon acid activity at constant ionic strength. As noted in the introduction, the evidence for first order dependence of rate on acid strength is unconvincing in many cases. Consequently, initial rates were obtained in salt concentrations high enough so that the acid which was added to adjust the pH contributes a negligible fraction to the ionic strength of the electrolyte, in order to determine the true order (13) of the reaction with respect to acid concentration. Since Initial Rate = $k c^n$, the slope of a plot of log Initial Rate vs. log c is the true order with respect to acid concentration. For 1 molal and 3 molal potassium chloride solutions the data, with probable errors, are listed in Table II, and

TABLE II

pH	Initial rate $\times 10^4$ (mgm. cm. ⁻² sec. ⁻¹)	
	1.0 molal KCl	3.0 molal KCl
1.6	10.9 \pm 1.0*	5.3 \pm 0.4
2.0	2.78 \pm 0.09	0.73 \pm 0.15
2.5	0.49 \pm 0.13	0.14 \pm 0.03
3.0	0.083 \pm 0.011	0.042 \pm 0.024

*Maximum probable deviation from the average values, as determined from repeat determinations and the weighing error.

are shown in Fig. 5. Definite curvature exists. The slopes indicative of first order and second order dependence are indicated. At low acid concentrations the order seems to be close to unity. At higher acid concentrations the order definitely increases, and in both cases approaches, if not exceeds, two. It is suggested that this behavior is another case (4), now believed by the authors to be common in film-controlled processes, in which internal dissolution of the film becomes increasingly important with increasing strength of the material which attacks and dissolves the film, in this case the acid. In a process which is diffusion controlled the rate of the controlling step is given by Fick's law, $dc/dt = D.A. dc/dx$, where dc/dt is the rate of diffusion, A the area of cross section, dc/dx the concentration gradient of the diffusing substance, and D

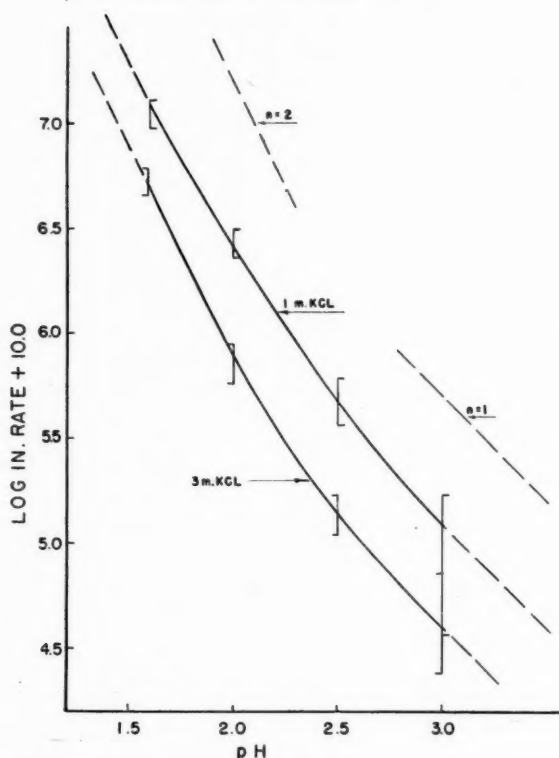


FIG. 5. Dependence of initial rate of dissolution of flat, horizontal faces upon acid strength in unstirred 1 molal and 3 molal potassium chloride. n is true order of the reaction with respect to acid activity. Temperature 25°C.

the diffusion coefficient of the diffusing substance. Since the diffusion coefficient reflects the structure of the surface film, the effect of acid on the film is of critical importance. In the case where the solution has low acid concentration the acid available at the film-solution interface would be small, and most would be expected to be used up dissolving the film at the film-solution interface. Also, in the low acid concentrations the stirring provided by the gas bubbles is small. Hence the amount of acid in the film, diffusing toward the electrode, would be small, and changes of the structure due to internal dissolution of the film would be small. Thus at low concentration of acid, since D would be essentially independent of acid concentration, the rate of the diffusion process would depend upon dc/dx only, and be first order with respect to acid concentration. In the case of stronger acid solution, however, owing in part to increased driving force for the cathodic process, which provides increased agitation by bubbles, and in part to increased diffusion and the onset of convection and eddy currents, acid molecules would get into the film and cause

internal dissolution of the film. The film thus weakened would now be more easily penetrable; the diffusion coefficient, D , is thus an increasing function, $F(c)$, of acid concentration. Hence at high acid concentrations the rate of the diffusion through the film is given by

$$dc/dt = A.F(c).dc/dx$$

and is seen to be of order greater than unity with respect to acid concentration. In terms of Müller's film theory, increased internal dissolution would be expressed as increased pore area per unit area of film.

In the case of the strongly acidic solutions, a possible method of supplying acid to the metal-film interface, alternative to pure diffusion aided by increased internal dissolution or reduced film thickness, could be diffusion augmented by other mass transport processes such as convection and local mass flow provided by the increased bubble formation and liberation. However, transport of acid directly to the metal surface by processes other than diffusion seems to be unlikely when consideration is taken of (a) the results of schlieren experiments on the "diffusion layer", (b) the state of our knowledge of the electrical double-layer, and (c) the success which has been achieved in describing mass transport along the surface in terms of kinetic theory of laminar flow. Pure diffusion aided by internal dissolution seems to account better for the facts obtained.

Presumably because of the poor solubility of magnesium hydroxide in 3 molal potassium chloride, the rate of dissolution of magnesium in 3 molal potassium chloride is less than in 1 molal potassium chloride. In terms of the above considerations this would mean that an effectively thicker or less porous film exists in 3 molal potassium chloride. One would expect that a small amount of internal dissolution in the film could exert more effect the more solidlike or the less porous the film. Consistent with this idea, greater curvature is noted in the curve (Fig. 5) for 3 molal potassium chloride, and the rate tends toward the higher order dependence at a lower concentration of acid than does the rate in 1 molal potassium chloride solutions.

The similar higher order dependence noted by Straumanis and Brakss (21) during studies of the dissolution of aluminum in sodium hydroxide solutions is quite conveniently explainable in terms of this internal dissolution theory, as were data obtained previously (4) on anodic processes occurring on zinc in caustic solutions. The similar data of Roald and Beck (19) on dependence of rate of dissolution of magnesium on acid strength are explainable in the same terms. Thus, the information obtained provides strong support for the internal dissolution theory and for the belief that the rate of the over-all process is either primarily or secondarily controlled by diffusion of acid into the film, since it is the rate of this step which controls the structure and the characteristics of the surface film upon which the rates of all the other mass transport processes are so critically dependent. However, it should be noted that it seems impossible to decide unequivocally, from the experimental information available in this or other researches, whether the slowest and rate determining step of the dissolution process is actually the diffusion of acid

into the film; the actual slowest step might indeed be any one of the other transport processes, one associated with hydrogen removal and liberation, perhaps, whose rate must depend so closely upon the structure of the surface film.

Magnesium Chloride Solutions

Further support for the postulate that the film is actually magnesium oxide or magnesium hydroxide is contained in information obtained on magnesium chloride solutions. Fig. 6 shows that, at the same pH over the same

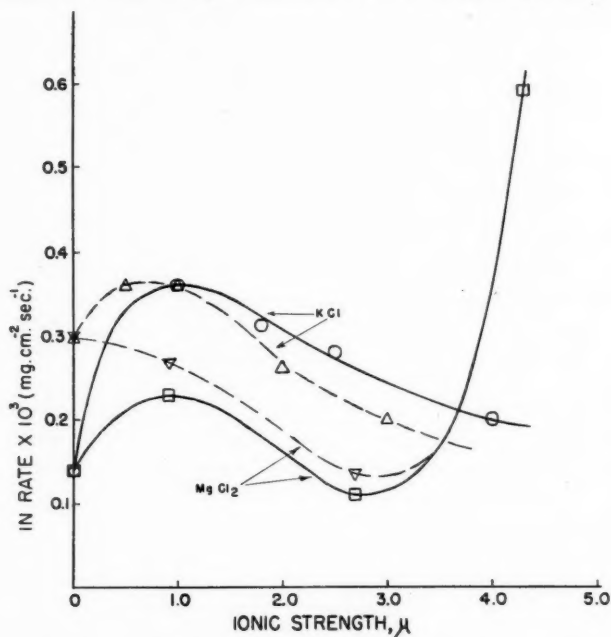


FIG. 6. Initial rate of dissolution as a function of ionic strength in potassium chloride solutions up to saturation, and in solutions of magnesium chloride of low concentration. Bold curves; flat, horizontal corroding faces. Broken curves; corroding rectangular bars.

range of ionic strength ($\mu = \frac{1}{2} \sum c_i z_i^2$), the rate of dissolution of magnesium follows closely the trends noted in potassium chloride solutions. The one notable difference is that all the rates in magnesium chloride solutions are lower. This further depression is interpreted as being a result simply of common ion depression of the solubility of magnesium hydroxide.

In Fig. 6, rates are shown for both round, flat, horizontal pieces and for oblong, vertical pieces. The difference, presumably a convection or an edge effect, shows up rather strikingly as a buffer to the various electrolyte effects. This phenomenon was not studied further.

At ionic strength 4.75 potassium chloride is saturated at 25°C., and depression of the rate with increasing ionic strength of salt was noted nearly up

to saturation. However, beyond ionic strength of about 3 in magnesium chloride solutions (that is, at concentrations greater than 1 molal), the rate of the dissolution process increases very rapidly with increasing concentration, and goes through another maximum. This is shown in Fig. 7, the data being listed in Table III. This behavior can also be explained in terms of the pro-

TABLE III

Molality of MgCl_2	Initial rate $\times 10^3$ (mgm. cm. ⁻² sec. ⁻¹) at 25°C.
0	0.15
0.31	0.23
0.90	0.11
1.44	0.59
2.26	1.15, 0.95*
3.03	1.38
4.00	1.48, 1.52*
5.44	1.13, 1.13*

*By hydrogen evolution. Each recorded initial rate by weight loss method is an average value of 4-10 experimental determinations.

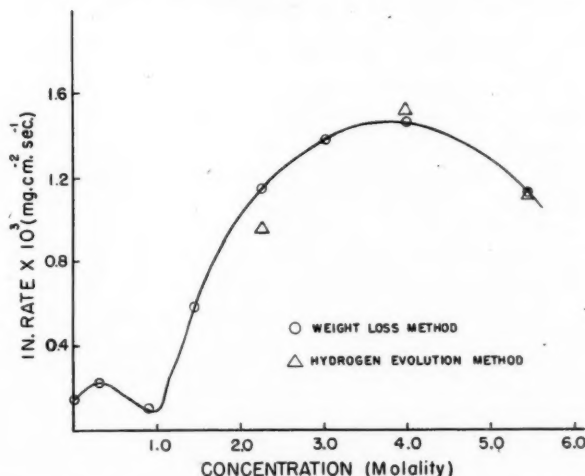
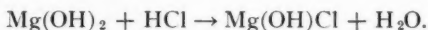


FIG. 7. Initial rate of dissolution of flat, horizontal corroding faces as a function of concentration of magnesium chloride, pH = 2.0, temperature 25.0°C. The curve below 1 molal magnesium chloride is enlarged in Fig. 6.

perties of magnesium hydroxide, for in this region of ionic strength the solubility of magnesium hydroxide is known to be augmented by the presence of magnesium salts. The values given by Robinson and Waggaman (20) for the solubility of magnesium oxide in aqueous magnesium chloride solutions as a function of magnesium chloride concentration follow very closely the sense of the rate values (Fig. 7) in the regions of concentration 1.0 to 4.0 molal

magnesium chloride. This enhanced solubility is presumably a result of the formation of the soluble oxychloride which was indicated by the solubility and potentiometric titration work of d'Ans and Katz (2). In this regard it is interesting to note that the greater the concentration of magnesium chloride used for the rate determination the more difficult it was to obtain an initial rate of reaction which actually referred to the starting pH. That is, in this region of concentration very little acid need be added to a magnesium chloride solution to adjust the pH to 2, and consequently very little reaction need occur before the pH had risen to 6 or 7. This region of pH, 2 to 7, seemed to be a potentiometric titration inflection point, presumably of the neutralization reaction



The amalgamation technique used by Hoar and Farthing (7) provided further evidence that (a) a surface film exists in magnesium chloride solutions of $\mu < 3$, and that (b) this surface film is increasingly more soluble or less solidlike in magnesium chloride solutions of concentration above $\mu = 3$. In a solution of 0.3 molal magnesium chloride a flat piece of magnesium would corrode away slowly and be untouched by droplets of mercury allowed to fall on the surface. In fact, the metal would be unattacked if left sitting on a pool of mercury, even when the solution was shaken vigorously in order that the magnesium be not held away from the mercury by hydrogen bubbles. In contrast, when the same experiment was done in 4 molal magnesium chloride, after a few seconds of corrosion amalgamation of the magnesium had started and the mercury attack was spreading over the surface. The surface was thus protected by a surface film in solutions of $\mu < 3$, and this protective film was either very weak or nonexistent in 4 molal magnesium chloride.

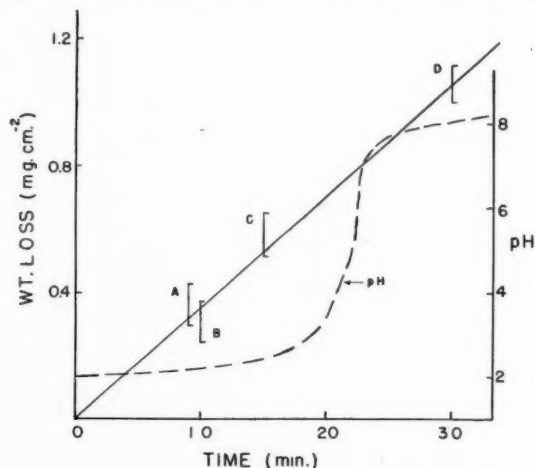


FIG. 8. In 1.44 molal magnesium chloride solution, weight loss and pH of solution vs. time. pH of each solution after the rate determination: A, 2.21; B, 2.25; C, 2.42; D, 8.1. Temp. 25°C.

The dependence of rate of the dissolution upon concentration of acid in those regions of salt concentration greater than 1 molal could not be determined directly because of the inflection point behavior noted above. However it was shown indirectly that the rate of the dissolution process is essentially independent of pH in this region; Fig. 8 shows weight loss - time data for 1.44 molal magnesium chloride, the highest concentration at which it was possible to be sure that the initial rate actually referred to $\text{pH} = 2$. The pH of the solution after the dissolution run had been done is noted for each determination. That a straight line, within the experimental error, passes through zero time and all the points must indicate that the rate is essentially independent of acid concentration, for if the pH dependence were strong, as in the case of $\mu < 3$ (Fig. 5), the weight loss vs. time curve would flatten off as time proceeds. Further actual measurements of the pH during dissolution in a solution of 1.44 molal magnesium chloride as a function of time of dissolution are dotted in to indicate the time dependence of pH of the solution during dissolution, the time base having been adjusted to correct for the necessary extra stirring since the two experiments could not be done simultaneously.

TABLE IV

Temperature (°C.)	Initial rate $\times 10^3$ (mgm. cm. ⁻² sec. ⁻¹) in 4 molal MgCl_2 , $\text{pH} = 2.0$
0.0	0.23 ± 0.015
25.0	1.48 ± 0.21
55.0	7.76 ± 0.69

In 4.0 molal magnesium chloride at $\text{pH} = 2$ the temperature coefficient of initial rate was found to be 11.2 kcal./mole (Table IV, Fig. 9). Apparently the complexing of the film substance is so strong and so fast that no effective surface layer in fact exists in these higher concentrations of magnesium chloride. In 4 molal solutions, where the rate is nearly independent of magnesium chloride concentration, independent of acid concentration, and the activation energy for the process is 11.2 kcal./mole, one must now be measuring a step which is not physical at all but rather one of the chemical-type steps relating perhaps to the complex formation reaction or to hydrogen discharge and evolution. King and co-workers noted apparent chemical control of the dissolution process in the dissolution of iron at extremely high linear velocity where the stirring is sufficient to dissolve the surface film, and also noted apparent chemical control of the dissolution of metals in solutions containing depolarizers. But the case reported here is believed by the authors to be the first case of chemical control noted with stationary metal pieces where the cathodic reaction is all hydrogen evolution.

Solubility data available indicate no maximum in the solubility of magnesium hydroxide at 4 molal, but rather a gentle increase in higher concentrations of magnesium chloride. The definite depression of the rate at concentrations

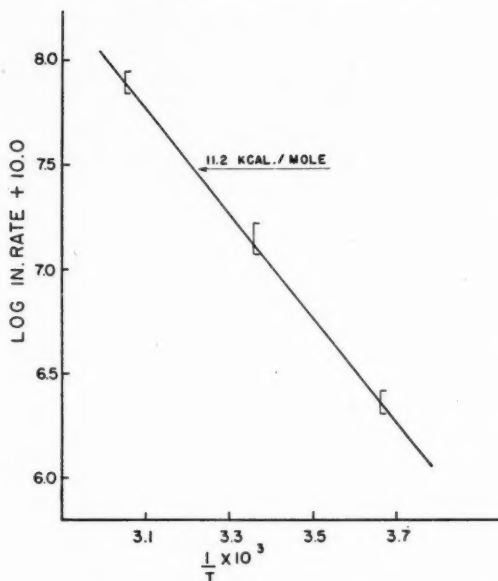


FIG. 9. Arrhenius plot of initial rates of dissolution of flat, horizontal faces of magnesium in 4.0 molal magnesium chloride. Initial pH = 2.0.

above 4 molal is interpreted tentatively as being due perhaps to salting-out of the complex in the vicinity of the electrode where the pH is high.

Mixed Potential Measurements

Measurements of corrosion potentials as measured against 1 molal silver-silver chloride electrodes are listed in Table V. Measurements were made on

TABLE V

Salt	Concentration (molality)	$E_{\text{Mg-Ag/AgCl}}$ (measured), volts	$E_{\text{Mg-hydrogen}}^{\text{mixed}}$ (corrected), volts	Corrosion rate $\times 10^3$ (mgm. cm. ⁻² sec. ⁻¹)
KCl	0	1.840	1.497	0.295
	0.5	1.890	1.700	0.36
	1.0	1.960	1.725	0.36
	2.0	1.967	1.749	0.26
	3.0	1.960	1.752	0.20
MgCl ₂	0	1.840	1.497	0.295
	0.31	1.790	1.62	0.23
	0.90	1.870	1.646	0.122
	1.44	1.93	1.73	0.58
	2.26	1.93	1.75	1.15
	3.03	1.92	1.77	1.38
	4.0	1.94	1.82	1.50
	5.44	1.91	1.83	1.13

oblong pieces of magnesium half submerged in the electrolyte. For potassium chloride solutions the points of the last two columns are plotted on a polarization diagram, Fig. 10, which shows the polarization of both local anodes and

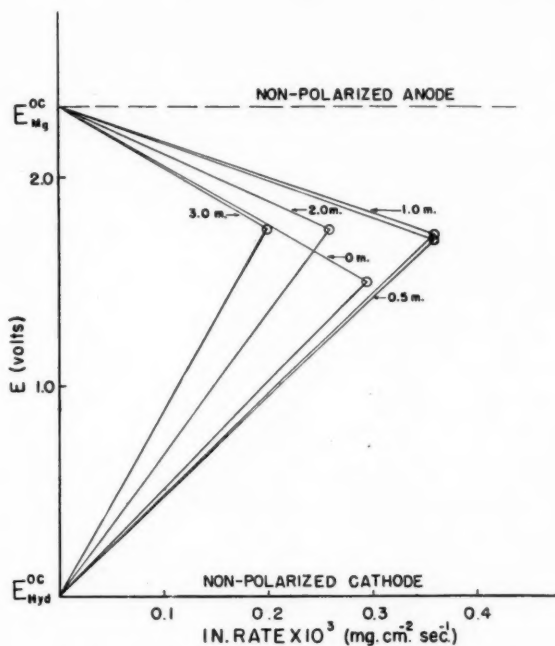


FIG. 10. Mixed potential - corrosion rate data for corroding rectangular bars of magnesium; pH = 2.0; temperature = 25°C. Straight lines joining E^{oc} to E^{mixed} are first approximations of the anodic and cathodic polarizations as a function of local corrosion current.

local cathodes, the mixed potential and the local current for autocorrosion. The information available in general on polarizations as functions of current indicates that in fact a curvature exists in the trace which joins the open circuit potential, E^{oc} , with the mixed potential, E^{mixed} . Since the curvature would not be expected to change markedly with change in concentration of solution, and since the curvature in the known systems is not large in any case, a first approximation is a straight line joining E^{oc} with E^{mixed} . For the hypothetical case where the local current could be controlled, then, the relative polarizations in different solutions at the same rate of corrosion can be estimated from the graph. The relative polarizations $E^{\text{oc}} - E$ obtained in this manner for local anodes and cathodes are shown plotted against ionic strength for both magnesium chloride and potassium chloride in Fig. 11. The ordinate is only relative, of course, since the values plotted are for one chosen current. Fig. 11 shows that the polarizations at local anodes and local cathodes as functions of ionic strength of the solutions express in other

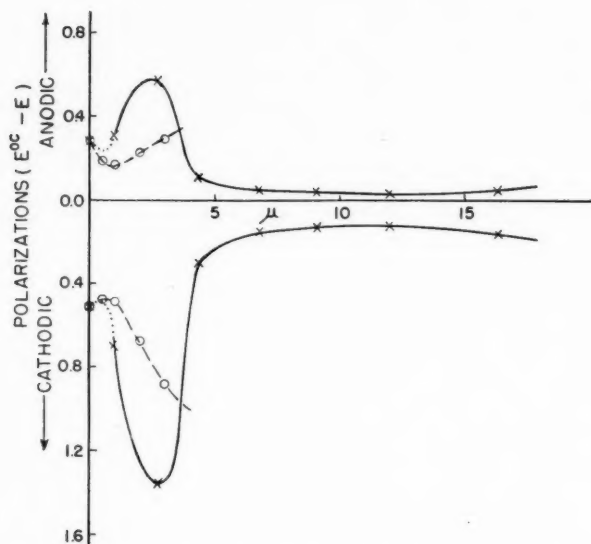


FIG. 11. Relative local anodic and cathodic polarizations on magnesium corroding in acidic ($\text{pH} = 2.0$) solutions of potassium chloride (O) and magnesium chloride (X) as a function of ionic strength of solutions. Values refer to local current of 1.0×10^{-4} mgm. cm^{-2} sec^{-1} .

terms the trends in the rate noted in Figs. 6 and 7. The extra depression of solubility of the magnesium hydroxide film by the presence of the common ion in magnesium chloride solution shows up markedly at $\mu \cong 2$; and the remarkable reduction of the polarizations at $\mu > 3$ is very evident. In all cases, the polarizations of the local cathodes are considerably greater than the polarizations of the local anodes, but this may be just an indication that the total area of the local cathodes is much less than the total area of the local anodes, that the cathode current density is higher than the anode current density.

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THE FRACTIONAL PRECIPITATION OF GR-S

THE EFFECT OF CONCENTRATION OF THE SOLUTION ON THE EFFICIENCY OF FRACTIONATION¹

By L. H. CRAGG AND D. F. SWITZER²

ABSTRACT

A careful study was made of the fractionation of GR-S (commercial poly(butadiene-co-styrene)) by stepwise precipitation, from solution in benzene, with the precipitant 50:50 (by volume) methanol-benzene. To determine the reproducibility of fractionation, particularly in the high-molecular-weight region, three runs were made with 2% solutions; and to determine the effect of concentration on efficiency, comparable fractionations were performed from solutions of three different concentrations—1, 2, and 3½ gm./100 ml. respectively. In each of the fractions the value of intrinsic viscosity, the viscosity slope constant β , and the viscosity-average molecular weight were determined. These provide conclusive evidence that in such a primary fractionation a much cleaner separation is accomplished from a dilute solution (1% or less).

INTRODUCTION

Although the various molecular species comprising a linear high polymer may differ in several respects, molecular chain length is usually much the most significant one. The distribution of chain lengths (and therefore of molecular weights) in a given sample depends on its history but is usually broad enough that for many purposes it is desirable or necessary to separate the sample into fractions more nearly homogeneous with respect to chain length. Although several means of accomplishing this are available (5), the one most commonly used is fractional precipitation (progressively decreasing the solvent power of the solvent).

Although there have been remarkably few studies of fractional precipitation per se, several of the many investigators who have used this means of obtaining fractions have stated that fractionation is most efficient when the solution is very dilute. Moreover, the theoretical treatments of solubility and fractional precipitation, developed in recent years by Schulz, Flory, Huggins, Gee, and Scott,* all tend likewise to the conclusion that the initial concentration of the solution should be low (less than 1%). Unfortunately, precipitation from such low concentrations requires more time, more materials, and more cumbersome apparatus. For these reasons, and because the conclusion was based on observations that were more or less incidental and on theories that embodied simplifying assumptions, Morey and Tamblin in 1946 made an experimental study of the effect of concentration on efficiency (16). They concluded that "the effect of initial concentration on the efficiency of fractionation by precipitation

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* Theories of fractionation are ably reviewed by Morey and Tamblin (17), Hildebrand and Scott (10), Bawn (1), and Frith and Tuckett (9).

is minor". The same conclusion was reached by Rehner (cited in Reference (17)) from his experience with fractionations of butyl rubber.

This contradiction between theoretical predictions and experimental results emphasized the need for further experimental work. Accordingly, we decided to make a careful test of the effect of concentration on the efficiency of the fractional precipitation of GR-S (poly(butadiene-*co*-styrene)) using benzene as solvent and methanol as precipitant. This polymer was chosen both because of its own importance and because it represents the rubberlike polymers, and benzene-methanol was chosen as the solvent-nonsolvent system because it is the one almost always used in fractionating GR-S.

EXPERIMENTAL

1. Materials

The polymer was normal production GR-S (poly(butadiene-*co*-styrene)) obtained from Polymer Corporation Ltd., Sarnia, a portion of lot S-2503. The analysis supplied with it was as follows:

Intrinsic viscosity	2.14 ± 0.02	Free fatty acid	$4.95 \pm 0.04\%$
Mooney viscosity	52.5 ± 1.0	Antioxidant	$1.53 \pm 0.03\%$
Total ash	$0.66 \pm 0.08\%$	ETA extract*	$7.34 \pm 0.05\%$
Soluble ash	$0.51 \pm 0.07\%$	Bound styrene	$23.5 \pm 0.1\%$
Free soap	$0.22 \pm 0.03\%$		

The polymer was stored in the dark in air. It was free of gel when received and showed no change in either gel content or intrinsic viscosity over the whole period of experimentation. It was used without purification.

The *antioxidant* used was phenyl- β -naphthylamine (PBNA), technical-grade material obtained from Polymer Corporation. For convenience in use, it was dissolved in benzene to form a 10% solution (gm./100 ml.).

The *solvent* was benzene, ASTM Industrial Grade, Steel Company of Canada, distilled and dried over sodium, b.p. 80.1°C ., n_D^{25} 1.49744, d^{25} 0.8739 gm./ml.

The *nonsolvent* was methanol, synthetic, Carbide and Carbon Chemical Co., used as received (since drying and distilling did not alter its refractive index), b.p. 64.7°C ., n_D^{25} 1.3262, d^{25} 0.7864 gm./ml.

The precipitant was a 50:50 (by volume) solution of the benzene and methanol, accurately prepared and kept in a ground-glass-stoppered bottle, $n_D^{25} = 1.4110$.

2. Apparatus

The *fractionation vessel* was a 1-liter Pyrex Squibb separatory funnel modified by the addition of a vertical side arm. The stem of the funnel was cut off just below the stopcock. Above it, the funnel was graduated for the first 100 ml. so that the volume of the precipitated phase could be measured (roughly) in the vessel. During precipitation the vessel was sealed with cork stoppers. Through the one in the side arm was inserted the tip of the burette from which

* Portion soluble in ethanol-toluene azeotrope.

precipitant was added; through the one in the neck of the funnel was inserted the shaft of the stirrer equipped with a grease seal to prevent the escape of vapor. During equilibration these stoppers were replaced with standard-taper glass stoppers.

The *viscometers* were of the Ostwald-Cannon-Fenske type, ASTM Series 50.

Two *constant-temperature baths* were used, a large one of the aquarium type for precipitating and equilibrating fractions and for viscosity measurements, and a smaller cylindrical glass jar for redissolving and reprecipitating fractions. In both, water was the bath liquid and its temperature was maintained at $25.0 (\pm 0.01)^{\circ}\text{C}$. by a cooling coil and heaters controlled by a sensitive thermoregulator.

3. Procedure

Preparation of Solutions

As noted above, the GR-S was used without further treatment. In preliminary experiments the polymer was extracted with ethanol-toluene azeotrope containing 10% water (12), but the product either contained varying amounts of extractant or, if drying conditions were rigorous enough to remove the extractant completely, varying amounts of insoluble gel. This separate extraction step was shown to be unnecessary because in each stage of the fractionation the extractable material remained in the supernatant liquid. (The precipitated phases were colorless—like solutions of extracted GR-S—and in one fractionation that was carried to completion it was found that the liquid from which no more polymer could be precipitated left, on drying, a residue corresponding closely in weight to the extractable material in the original sample.)

A solution was prepared by allowing the sample of polymer, cut into fine pieces, to stand in contact with benzene in the dark, with occasional gentle shaking. After dissolution was complete, the solution was filtered through a coarse sintered-glass disk, and its density determined. Its concentration was then determined by slowly evaporating aliquot portions, the final drying to constant weight being done in an oven at 100°C .

Fractionation Procedure

About 400 ml. of the solution was introduced into the fractionation vessel and allowed to come to thermal equilibrium in the bath at 25.0°C . Then, with vigorous stirring, the precipitant was added, slowly enough to prevent the formation of curds of rubber, until the solution became just turbid enough that the stirrer shaft could not be seen when viewed in line with a 100-watt bulb behind the bath. (This criterion was only a rough guide, especially with the high fractions, but could be modified with experience to make possible the obtaining of fractions of the desired size.)

The vessel was then transferred to the smaller bath, and its contents were heated slowly, with stirring, until the cloudiness just disappeared and then cooled slowly to 25.0°C ., with constant stirring to maintain near-equilibrium conditions. The system was left undisturbed at this temperature until the two liquid phases had separated completely (24–46 hr.) and the denser precipi-

tated phase ("coacervate") was drawn off into a weighed volumetric flask, with suitable precautions to ensure an uncontaminated "precipitate". (The first three or four fractions separated so slowly that it was better to make a first rough separation and then replace the vessel in the bath for several hours to allow the rest of the very viscous coacervate to drain down from the sides.)

The coacervate was immediately weighed, treated with antioxidant (0.1 to 0.4 ml. of the 10% solution of PBNA), and diluted with benzene to a volume of 100 ml. After the weight, and hence the density, of this solution was determined, weighed aliquot portions were carefully evaporated to determine the concentration of polymer in the solution and therefrom the weight of polymer in the fraction.

Various methods of obtaining the fraction free of solvent were tried, including freeze-drying, but all resulted in the formation of insoluble gel, particularly in the first few fractions. Fortunately, a solution of the fraction was all that was necessary for our purpose—intrinsic viscosity determination. When the solution was stored in tightly-stopped containers in the refrigerator no change in the polymer could be detected by intrinsic viscosity determinations, even after several months.

Viscosity Determinations

The solution containing the fraction was diluted with benzene to obtain at least three and usually four solutions ranging in concentration from 0.35 to 0.05 gm./100 ml. of solution. The flow time, t_s , of each of these solutions was measured with the usual care (7), and values of reduced flow time $(t_r - 1)/c$, and inherent flow time, $(\ln t_r)/c$, calculated (2). The intrinsic flow time $[t]$ was obtained by plotting both of these against concentration and extrapolating to a common point at $c = 0$. Kinetic energy corrections were not applied, but because the flow times for benzene, t_0 , in the three viscometers were 187.4, 166.2, and 162.5 sec. the difference between values of $[t]$ and of intrinsic viscosity $[\eta]$ will be very small. (Because the fractions were never dried, a small amount of methanol was present in these solutions, even in the solutions obtained by diluting the liquid fractions to 100 ml. The concentration of methanol was, however, never higher than 1.8%—as determined refractometrically—and was usually much lower. Because of this low concentration and because the later dilutions were made with pure benzene, the effect on the intrinsic viscosity would be negligible.)

RESULTS

After three preliminary fractionations were performed to determine the most suitable procedures; to develop technique, and to acquire experience, careful fractional precipitation was begun from solutions of different concentrations. The first of these fractionations, run 4, was from a solution whose original concentration was 1.92 gm. whole polymer per 100 ml. solution. Fourteen fractions were obtained comprising 97% of the copolymer originally present. Then fractionations from solutions with concentrations of 1.00, 2.03, and 3.66% respectively (runs 5, 6, and 7) were begun. The second of these

was terminated by accident after four fractions had been obtained and another fractionation (run 8), starting with a concentration of 2.10%, was begun. Because of the pressure of time, none of these fractionations were completed, but they were carried far enough for our purpose since improvements in the efficiency of fractional precipitation will affect principally the first (highest-molecular-weight) fractions.

Table I is a summary of further details regarding these fractionations. The weight of copolymer was calculated from that of the GR-S (whole polymer)

TABLE I
DETAILS OF FRACTIONATIONS

Run	Concentration of soln. (gm./100 ml. soln.)		Weight (gm.)		Proportion pptd. (wt. %)	Number of fractions
	Original	At initial pptn.	GR-S (whole sample)	Copolymer		
4	1.92	1.61	7.68	7.12	97.0	14
5	1.00	0.84	3.97	3.68	73.1	15
6	2.03	1.71	8.04	7.45	22.1	4
7	3.66	3.10	14.4 ₄	13.4 ₃	68.3	14
8	2.10	1.76	8.32	7.71	42.5	8

by subtracting 7.34%, the portion soluble in the ethanol-toluene azeotrope. Q , the cumulative proportion (% by weight) of copolymer precipitated, is based on this weight. Table II is a materials balance for the completed fraction-

TABLE II
MATERIALS BALANCE—RUN 4

	Starting material			Products	
	Wt. (gm.)	% (by weight)		Wt. (gm.)	% (by weight)
ETA extractables	0.56	7.34	Copolymer in fractions	6.91	90.1
Copolymer	7.12	92.66	Residue	0.75	9.8
	7.68	100.00	Unaccounted for	7.66	99.9
				0.02	0.1
				7.68	100.00

ation. The residue, the portion that could not be precipitated from solution but was recovered on drying, probably consists of the portion extractable with the ETA and copolymer species of very low molecular weight. The remainder of the original sample, a very small proportion, may be attributed to losses in handling fractions or to errors in concentration determinations.

In Table III are recorded data concerning the individual fractions. For each the viscosity-average molecular weight \bar{M}_v was calculated from the intrinsic flow time $[\eta]$ assuming it to be equal to the intrinsic viscosity $[\eta]$ and using the equation of Scott, Carter, and Magat (18). Q is again the cumulative percentage of copolymer precipitated and S is a corrected Q obtained for each

TABLE III
EXPERIMENTAL DATA FOR THE FRACTIONS OBTAINED IN FRACTIONAL PRECIPITATIONS
FROM SOLUTIONS OF THREE DIFFERENT CONCENTRATIONS

Run	Original concentration (gm./100 ml.)	Fraction	$[\eta]$	\bar{M}_v ($\times 10^{-4}$)	Q (%)	S (%)
4	1.92	1	4.06	63.5	8.82	4.41
		2	3.74	56.0	17.26	13.04
		3	3.53	51.5	20.86	19.06
		4	3.32	46.9	25.66	23.26
		5	2.98	39.9	28.99	27.33
		6	2.61	32.8	33.79	31.39
		7	2.31	27.4	41.15	37.47
		8	1.94	21.1	47.11	44.13
		9	1.70	17.3	54.40	50.76
		10	1.36	12.4	63.99	59.20
		11	1.07	8.7	74.00	69.00
		12	0.82	5.8	83.34	78.67
		13	0.63	4.0	89.83	86.59
		14	0.42	2.1	97.02	93.43
5	1.00	1	4.91	84.1	3.55	1.78
		2	4.83	82.0	8.53	5.99
		3	4.36	70.1	12.99	10.76
		4	3.78	57.0	17.23	15.11
		5	3.72	53.8	20.74	18.98
		6	3.23	45.1	24.06	22.40
		7	3.12	42.8	28.63	26.34
		8	2.86	37.5	33.64	31.14
		9	2.36	27.0	39.81	36.73
		10	2.02	22.4	45.98	42.90
		11	1.68	17.0	52.15	49.07
		12	1.52	14.7	57.15	54.65
		13	1.33	12.0	63.42	60.29
		14	1.13	9.4	68.75	66.09
		15	0.94	7.1	73.13	70.94
6	2.03	1	4.24	67.6	6.70	3.35
		2	4.08	64.0	12.70	9.70
		3	3.86	58.8	16.48	14.59
		4	3.42	49.1	22.07	19.28
7	3.66	3	3.07	41.8	8.79	4.40
		2	2.97	39.8	15.21	12.00
		5	2.93	39.0	21.39	18.30
		1	2.87	37.8	28.84	25.12
		4	2.81	36.7	31.83	30.34
		6	2.73	35.1	36.79	34.31
		7	2.68	34.1	41.86	39.33
		8	2.48	30.5	46.00	43.93
		9	2.33	27.7	50.29	48.15
		10	2.15	24.5	54.08	52.19
		11	2.08	23.4	57.99	56.04
		12	1.95	21.2	62.38	60.19
		13	1.71	17.5	65.56	63.97
		14	1.61	16.0	68.33	66.95
8	2.10	1	4.18	66.1	7.97	3.99
		2	4.03	62.5	14.99	11.48
		3	3.82	57.8	21.28	18.14
		4	3.52	51.3	26.23	23.76
		5	3.18	44.0	30.37	28.30
		6	3.00	40.4	34.19	32.28
		7	2.72	35.0	38.93	36.56
		8	2.47	30.3	42.46	40.70
Whole polymer			2.15	24.5		

fraction by adding half the percentage of copolymer in that fraction to the Q for the preceding fraction. (This procedure is based on the assumptions that the molecular-weight distribution in each fraction is symmetrical and that in any fraction none of the polymer species are of molecular weight greater than the average molecular weight of the fraction next below—or above—it.) It should be noted that the values of Q , and therefore of S , are calculated in the

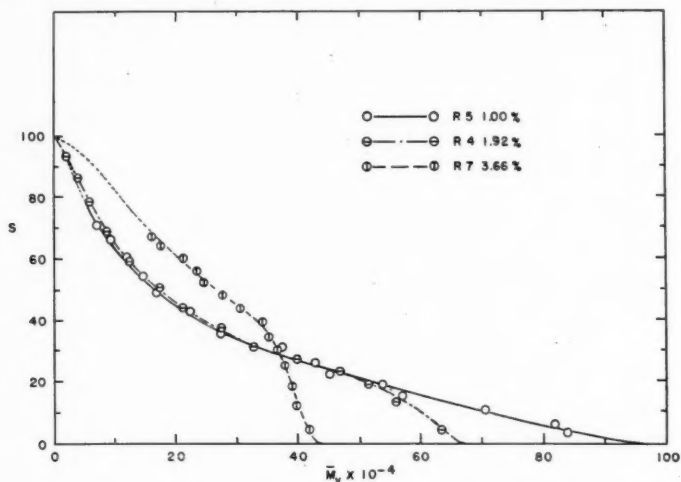


FIG. 1. Integral molecular-weight distributions obtained in fractionations from solutions of three different concentrations. System: GR-S-benzene-methanol.

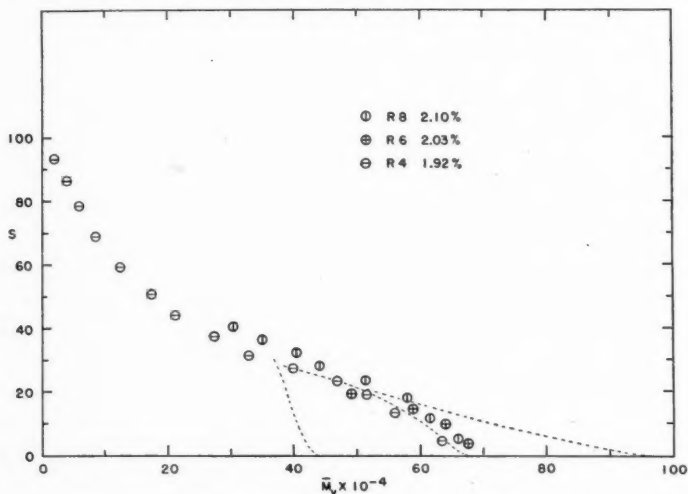


FIG. 2. Integral molecular-weight distributions obtained in three fractionations (two of them incomplete) from 2% solution.

order of decreasing average molecular weight of the fractions rather than in the order of precipitation of the fraction.

The data of Table III for runs 4, 5, and 7 are plotted in Fig. 1 to give integral molecular-weight distribution curves for the three different concentrations. In Fig. 2 are plotted the data for runs 4, 6, and 8 to show the degree of reproducibility of results attained at one concentration. In Fig. 3 are the

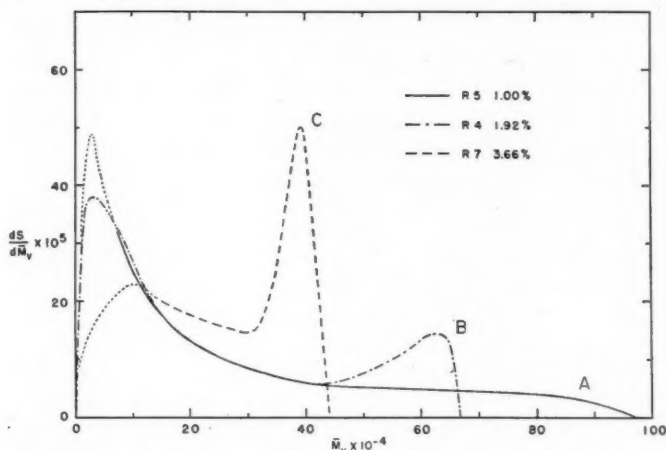


FIG. 3. Differential molecular-weight distribution curves obtained when fractionating at three different initial solution-concentrations.

three differential distribution curves corresponding to the three curves of Fig. 1 and obtained from them by drawing tangents and plotting their slopes, $dS/d\bar{M}_v$. Since only run 4 was completed, each of the other curves in Fig. 1 has been extrapolated, as indicated by the dotted portion in the low-molecular-weight region, to $S = 100\%$. The corresponding portions of the differential curves in Fig. 3 are similarly indicated. (The extrapolations in Figs. 1 and 3 were made having due regard to the usual shape of such curves and to the requirement that the total area under each of the differential distribution curves should be the same. The higher-molecular-weight regions of these curves are the most significant for our purposes; differences in those regions will, of course, be reflected by differences in the remainder of the curves, for low-molecular-weight species that come down in the first fractions cannot come down when they should in the later fractions.)

DISCUSSION

It is evident from Figs. 1 and 3 that the efficiency of fractionation is considerably affected by the concentration of the solution. The effect is particularly noticeable in the high-molecular-weight range, as would be expected. Fractionation from 1% solution reveals species of molecular weight over 900,000 whereas at 2% and 3½% the apparent upper limit of molecular weight is 700,000 and 450,000 respectively.

The differences between the distribution curves in Fig. 1 are much too marked to be attributed to experimental error. As is indicated in Fig. 2 by the scatter of the points (for three runs at about the same concentration) the experimental error is by no means insignificant. But particularly in the high-molecular-weight region where the effects of poor separation will be most evident, these points are much less separated than are the curves of Fig. 1 (reproduced here as dotted lines) for the 1%, 2%, and 3 $\frac{2}{3}$ % runs.

The effect of concentration on efficiency is even more noticeable in the differential distribution* curves of Fig. 3. These are, of course, derived from the integral curves of Fig. 1 and therefore their shape depends on the choice of lines drawn through the experimental points of Fig. 1. Nevertheless, the differences between the three curves are too great to be dismissed. The shape of curve A is much as would be expected from theory and very similar to that of distribution curves obtained in careful fractionations of another sample of GR-S (Polymer, lot S-2834) by fractional precipitation (14) and by the so-called "coacervate method" (13). By contrast, there is an unmistakable second peak in curve B (2%) at $\bar{M}_v = 650,000$ and a very pronounced one in curve C (3 $\frac{2}{3}$ %) at $\bar{M}_v = 400,000$. These peaks are certainly spurious; they are due to low-molecular-weight species which, precipitating with the high-molecular-weight species, both increase the weight of the top fractions and decrease their viscosity-average molecular weight. As the efficiency of fractionation increases, this peak decreases in height and moves to higher molecular weights. Its near absence in curve A indicates that fractionation from 1% concentration (performed as described above) is efficient enough for all but the most precise work.

The order of precipitation of the fractions provides additional evidence of decreased efficiency of fractionation at higher concentrations. From the 1% and 2% solutions the fractions come down in the order of decreasing intrinsic viscosity, as they are supposed to do. But from the 3 $\frac{2}{3}$ % solution the first fraction was third in (decreasing) order of intrinsic viscosity and the subsequent ones were, by this arrangement, numbers 2, 5, 1, and 4. Only with fraction 6 was the normal order attained. (See Table III.)

The viscosity behavior of the fractions, too, indicates differences in efficiency. In Fig. 4 are plotted, side by side for purposes of comparison, the inherent viscosity vs. concentration curves for the three fractionations of Fig. 1, i.e., runs 5, 4, and 7. Two different effects are noticeable. One is the increase in intrinsic viscosity for the corresponding top fractions and the resulting widening in the spread of intrinsic viscosities. This is the effect already discussed above, as revealed in distribution curves. The second is almost equally obvious but more difficult to describe. Ordinarily, that is with fractions obtained from a polymer comprised of linear species, the slopes of the lines in such a figure would all conform to the expression $-\beta[\eta]^2$, where β is a "slope constant" having the same value over a wide range of molecular weights.*

* The equation that fits all such lines is that of Mead and Fuoss (15)

$$(\ln \eta_r)/c = [\eta] - \beta[\eta]^2 c.$$

This may be compared to the Huggins equation (11)

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c.$$

The parameters β and k' are related by the equation $k' = 0.50 - \beta$ (8).

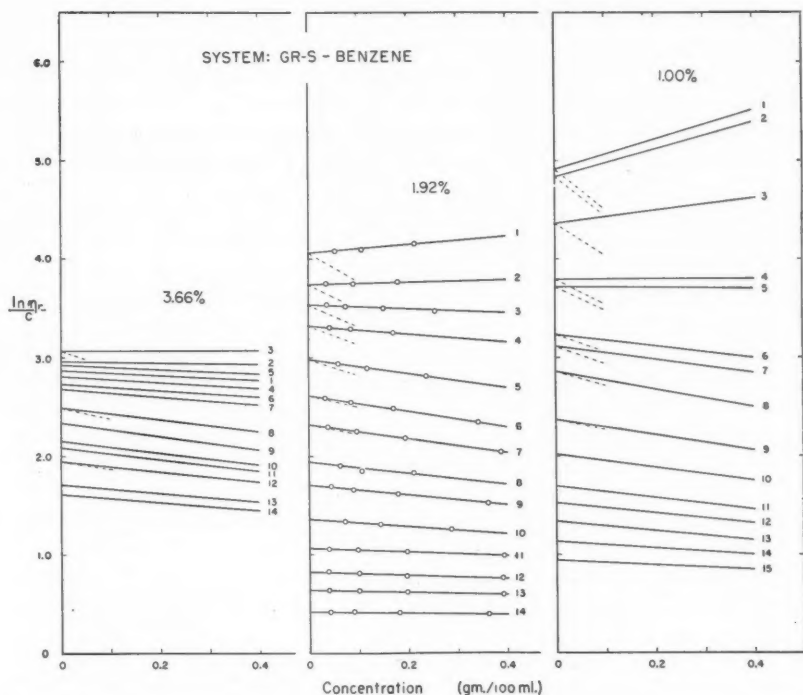


FIG. 4. Inherent viscosity vs. concentration curves for the fractions obtained in the three fractionations at different concentrations. (Actual points are plotted for the 1.92% fractionation to indicate the precision of measurements. Dotted lines indicate the slope corresponding to a constant value of β equal to that for the lower fractions.)

This means that at higher and higher intrinsic viscosities the slopes should be more and more negative, as indicated by the dotted lines in Fig. 4. With this polymer, however, the slope becomes more negative, then less and less negative and, finally, positive. This change corresponds to a progressive decrease in β (or increase in k'). It can be satisfactorily accounted for in terms of branching in the molecules, the degree of branching increasing with molecular weight (for further discussion of this effect, see References 6, 3, 4). The top fraction from the most concentrated solution has both a lower intrinsic viscosity and a less positive slope than the top fraction from the least concentrated solution. This suggests again that in fractionating at higher concentrations the species that are of highest molecular weight—and that are most branched—become more contaminated with species of lower molecular weight and lesser branching. If one compares fractions of approximately equal intrinsic viscosity (#5 at 3.3%, #5 at 2%, #8 at 1%), the fraction obtained at the lowest concentration appears to contain the least branching, but this is because here the species that are most highly branched have come down where they should, in the highest fractions. In other words, fractionation is most efficient at the lowest concentration.

The increased efficiency of fractionation at lower concentrations may be attributed to at least two factors. The first is entanglement. Long randomly-kinked molecules in precipitating are bound to carry shorter molecules down with them. The fractionation procedure is designed to minimize this effect, through redissolving, slow uniform reprecipitating, and long equilibrating, but it cannot be wholly avoided. The effect should be greater with the large molecules (the first fractions), with the more highly branched molecules (the first fractions again), and in higher concentrations.

The second factor is the distribution of polymer species between the two liquid phases. According to theory, low-molecular-weight species will be present in both phases, the highest-molecular-weight species chiefly in the coacervate, and this contamination of the high with the lower will be minimized by making the volume ratio (supernatant liquid to coacervate) as high as practicable. This can be accomplished either by increasing relatively the volume of the supernatant liquid (precipitating the same proportion of polymer from a more dilute solution) or by decreasing relatively the volume of the coacervate (precipitating a smaller proportion of polymer from a solution of the same concentration). In order to obtain the same number of (equal) fractions from a 2% solution as from an equal volume of 1% solution one would have to precipitate coacervates twice as voluminous.* In order to keep the volume ratio the same it would, therefore, be necessary to take twice as many fractions from 2% as from 1% solution. This is all very well in theory; in practice, doubling the concentration makes it much more difficult even to obtain the same number of fractions as before. (For example, in these experi-

TABLE IV
SIZE OF FRACTIONS OBTAINED (CALCULATED AS WEIGHT FRACTION
OF RUBBER IN THE ORIGINAL POLYMER SAMPLE)

Fraction	w_x		
	Run 5 (1.00%)	Run 4 (1.92%)	Run 7 (3.66%)
1	3.55	8.82	8.79
2	4.98	8.44	6.42
3	4.46	3.60	6.18
4	4.24	4.80	7.45
5	3.51	3.33	2.99
6	3.32	4.80	4.96
7	4.57	7.26	5.07

ments our aim was to make all fractions about the same weight fraction of the original sample, namely, about 0.04 or 0.05. The data of Table IV indicate that we were successful at 1% and, except for the first two fractions, at 2%; at 3 $\frac{2}{3}$ % the variation in size is much greater. This control of fraction size was

* The assumption is made that the concentration of polymer in the coacervate is the same, or very nearly so, in two experiments. Actually, the concentration in the first coacervate from our run 5 ($c = 1.00$) was 3.9 gm./100 ml. and in the first coacervate of run 4 ($c = 1.92$) it was 4.1 gm./100 ml.

achieved fairly readily at 1%, with difficulty at 2%, and only by exercise of considerable effort, time, and patience at the highest concentration.) Hence, although maintaining the same volume ratio at different concentrations might have revealed less ambiguously the effect of concentration alone, the experiment as we performed it—i.e., taking off equal numbers* of fractions at different concentrations—was better designed to answer the practical question: what is the optimum concentration for convenient and efficient fractionation.

Our conclusions differ markedly from those of Morey and Tamblyn (16). But we believe their conclusions are not justified by their data. In both their fractionations and especially in that of the copolymer, there was noticeably better separation at high molecular weights from the more dilute solution (see Figs. 1 and 2, Reference 16). And this in spite of the fact that in both fractionations they took fewer fractions from the more dilute solution. With the copolymer, 14 fractions were taken from the more concentrated (1.0%) solution and only six from the more dilute one (0.2%), seven fractions being required to precipitate half the polymer from the 1.0% solution but only two fractions to precipitate that proportion of the polymer from the 0.2% solution. Had they taken the same number of fractions at the two concentrations—particularly in the high-molecular-weight region—their distribution curves would probably have indicated an even greater difference in the efficiency of fractionation at the two concentrations.

ACKNOWLEDGMENTS

We wish to express our thanks to Mr. T. H. Murray and Mr. J. A. Manson for their assistance in some of the experimental work and to Mr. G. R. H. Fern for the data of Table V. We are also grateful to Polymer Corporation for providing materials, to the Research Council of Ontario for financial assistance (in the form of a scholarship for D.F.S.), and to the Associate Committee on Synthetic Rubber Research of the National Research Council of Canada for a grant in aid of the research.

* It may be objected that the decreased efficiency of separation of the two top fractions of run 4 ($c = 1.92\%$) as compared with run 5 ($c = 1.00\%$) may be due in large part to the fact that in run 4 the first two fractions are much larger. However, in runs 4 and 7 ($c = 1.92$ and 3.66%) the first two fractions are of comparable size and yet the efficiency of separation is still quite different. Moreover, in parallel fractionations of another sample of GR-S from two solutions of concentrations 1% and 2% respectively the difference in the efficiency of separation of the top fractions was about the same as here, even though the relative size (weight fraction) of the fractions was kept the same. See Table V.

TABLE V
PARTIAL FRACTIONATION OF ANOTHER GR-S SAMPLE
FROM 1% AND FROM 2% SOLUTION TAKING FRACTIONS OF
(APPROXIMATELY) EQUAL WEIGHT FRACTION

Fraction	1%		2%	
	w_x	$[\eta]$	w_x	$[\eta]$
1	3.96	5.44	3.36	4.47
2	4.12	5.17	4.08	4.15
3	3.48	4.54	5.80	4.13
4	3.75	4.44	4.00	3.23

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NOTE

THE OXIDATION OF FERROUS SULPHATE BY γ -RAYS—
THE TEMPERATURE COEFFICIENT OF AIR-SATURATED SOLUTIONS*

BY T. J. HARDWICK

The effect of temperature on the yield of ferric ion in the radiation-induced oxidation of ferrous sulphate in air-saturated 0.8 *N* sulphuric acid has been neglected by most radiation chemists, although the temperatures at which irradiations have been made range from 12° C. (4) to 25° C. (2). In view of the widespread use of this system in radiation actinometry, it is important to ascertain whether this neglect of temperature corrections is justified.

Previous experimental work on this matter was done by Minder (3), who reported no temperature coefficient, and by Dewhurst (1) who found an activation energy of 900 cal. Minder does not report the lower limits for his experimental results, while Dewhurst used apparatus which gave him considerable deviation from mean values. In view of this disagreement, it was considered worth while to reinvestigate the effect of temperature on the γ -ray oxidation of ferrous ion in 0.8 *N* sulphuric acid.

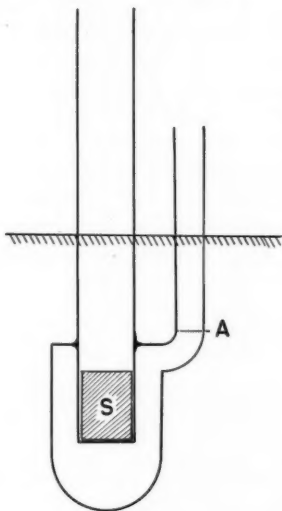


FIG. 1. Irradiation cell.

The apparatus in which the solution was irradiated was a well-type cell shown in Fig. 1. Ferrous sulphate (10^{-3} *M*) in 0.8 *N* sulphuric acid was added to the cell up to the indicated mark *A* (volume = 21 ml.). The cell was then

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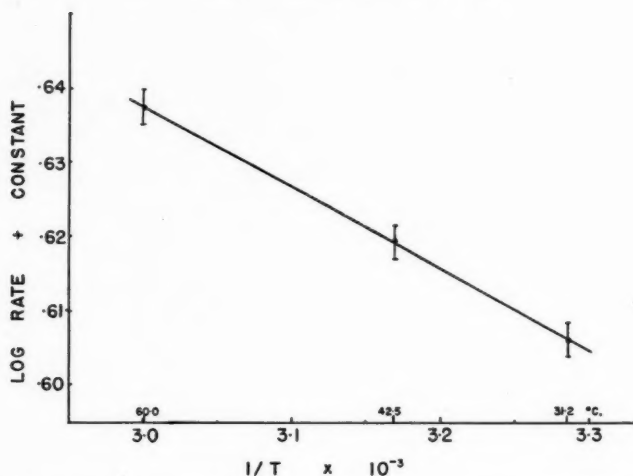


FIG. 2. Plot of log rate of reaction against the reciprocal of the absolute temperature.

immersed in a constant temperature bath to the level shown. When the sample reached bath temperature a 500 mc. Co^{60} source in the form of a right cylinder was dropped into the well. At the end of the irradiation (usually overnight) the source was removed and the solution allowed to come to room temperature before analysis. The amount of oxidation was determined by analysis for ferrous ion, using the *o*-phenanthroline method. At least six runs were made at each temperature.

Unirradiated samples were maintained at each temperature for corresponding periods. Corrections for the thermal reaction (small in all cases) were made to the rates of radiation-induced oxidation. As the γ -ray absorption per unit volume of 0.8 *N* sulphuric acid decreases with increase in temperature, suitable corrections were applied to the measured rates of oxidation.

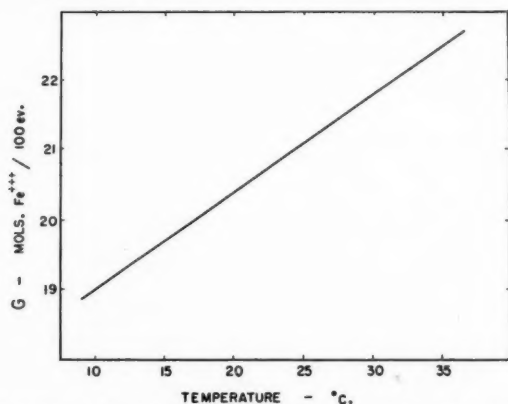


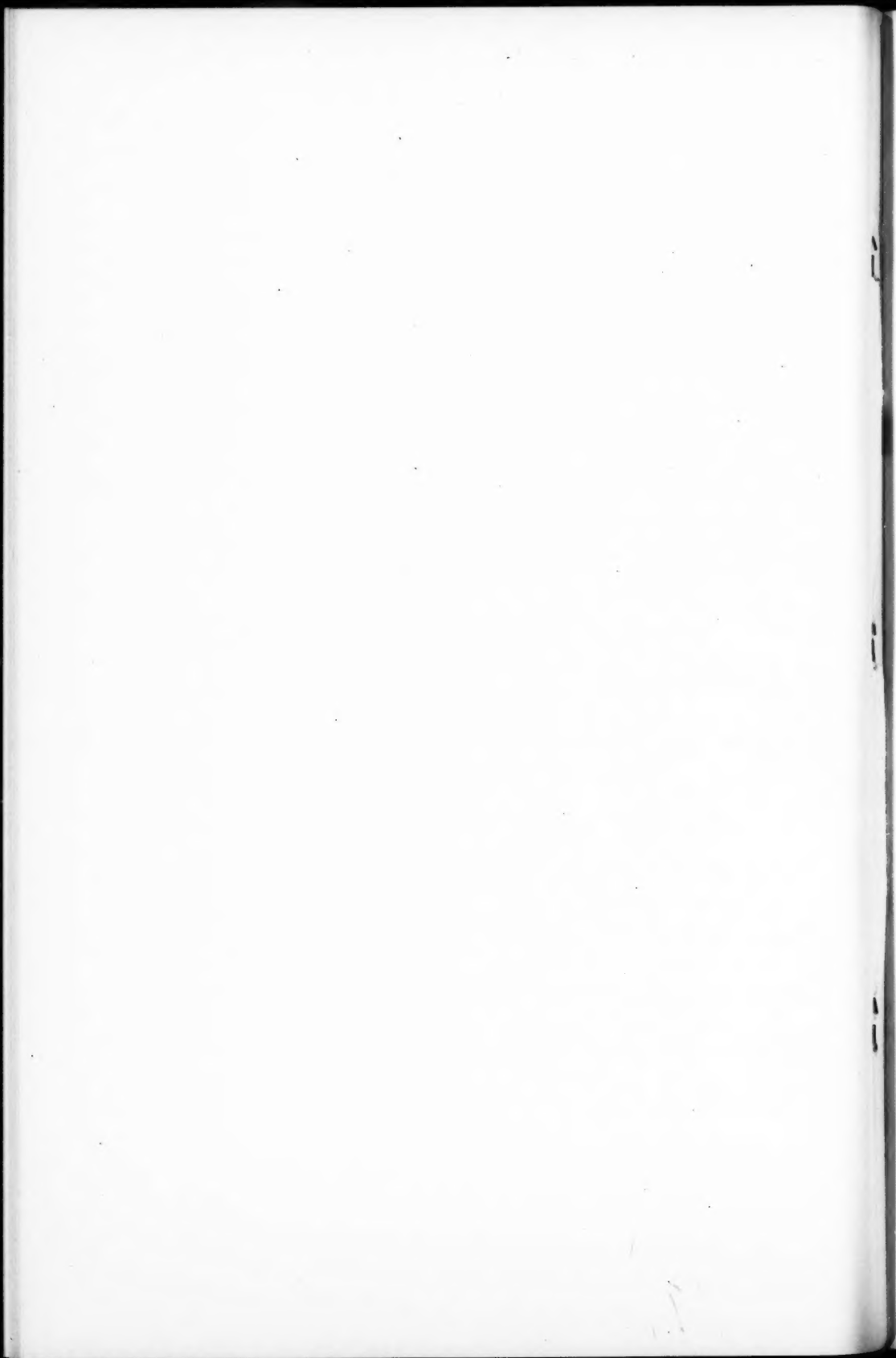
FIG. 3. Values of $G_{\text{Fe}^{+++}}$ at various temperatures. ($G = 20.4$ at $20^\circ \text{C}.$)

The results at three temperatures (31.2, 42.5, and 60.0° C.) are shown in Fig. 2. The length of the vertical lines at each temperature indicates the standard deviation. The temperature coefficient calculated from these data is 550 ± 50 cal., a value intermediate between that of Dewhurst and that of Minder.

Although small, this temperature coefficient must be considered if this system is used as a radiation actinometer; a difference of 5° C. will result in a 2% change in rate. In Fig. 3 the yield of ferric ions is plotted as a function of temperature, assuming $G = 20.4$ mols./100 ev. at 20° C. On the other hand, the magnitude of this temperature coefficient is such that it is difficult to assign it to any of the processes which occur during the γ -ray-induced oxidation of ferrous ion.

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VOLUME 1

BOOK 1

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